# Beyond 2-State Systems

For physical quantity $Q$, corresponding to operator Q, there exist eigenstates $|q_1\rangle$, $|q_2\rangle$, …, $|q_n\rangle$, …, with eigenvalues $q_1$, $q_2$, …, $q_n$, …, respectively. Thus, an arbitrary state

$$|\psi\rangle = \sum_n c_n |q_n\rangle .$$

If the number of eigenstates is $N$, $|\psi\rangle$ is in an $N$-dimensional Hilbert space; $N$ may be $\infty$.

In the basis made of its own eigenstates, operator Q is a diagonal matrix.

$$\mathrm{Q} = \begin{pmatrix} q_1 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & q_N \end{pmatrix}.$$

(How do you write $|q_n\rangle$ in the 1-column matrix form? How about the corresponding bra?)

Obviously,

$$\langle Q \rangle = \sum_n |c_n|^2 q_n = \langle \psi | Q | \psi \rangle .$$

Note: As in the 2-state case, $\langle Q \rangle = \langle \psi | Q | \psi \rangle$ regardless of the choice of basis, as rules of vectors hold true regardless of the coordinate system.

## Energy and time evolution of a quantum system

Energy $E$ is such a special quantity that we give its operator a special name, the Hamiltonian H, with eigenvalues $E_0, E_1, E_2, \ldots, E_n, \ldots$, corresponding to eigenstates $|0\rangle, |1\rangle, \ldots, |n\rangle, \ldots$ Thus we have the eigenvalue equation

$$\mathrm{H}|n\rangle = E_n|n\rangle.$$

An energy eigenstate (i.e. a state with a definitive energy), $|n\rangle$, evolves in time following

$$|n(t)\rangle = e^{-i\frac{E_n}{\hbar}t}|n(0)\rangle = e^{-i\omega_n t}|n(0)\rangle, \text{ where } \omega_n = E_n/\hbar.$$

For a system in an energy eigenstate (i.e. a state with a definitive energy), $|n\rangle$, this phase evolution has no observable physical consequences. The eigenstates of H are called stationary states.

For a system in a state that is a linear combination (superposition) of stationary states, $|\psi\rangle = \sum_n c_n|n\rangle$, each term evolves at a different frequency thus beating happens.

This idea can be expressed in the matrix form, $|\psi(t)\rangle = \mathrm{U}(t)\,|\psi(0)\rangle$, where $\mathrm{U}(t)$ is a diagonal matrix with the $n$th diagonal element being $e^{-i\omega_n t}$ in the basis of $|0\rangle, |1\rangle, \ldots, |n\rangle, \ldots$

(We label eigenvalues and eigenstates with integers starting with 0 for the ground state.)

Too abstract? We have illustrated the same principles using a simple 2-state system example.

# Quantities with continuous eigenvalues

A state $|\psi\rangle$ of a quantum system is in an $N$-dimensional Hilbert space; $N$ may be $\infty$.

The spectrum of the eigenvalues may even be continuous!

Let's now consider the position of a particle in 1D space (for simplicity).
The positions is $x$, which is continuous.

We paused mid this slide on Tue 2/7/2023.

Let $|x\rangle$ be the state in which the particle is localized at $x$.

For a 2-state system, an arbitrary state $|\chi\rangle = c_0|0\rangle + c_1|1\rangle$.

More general than spin up and down

For an n-state system, an arbitrary state $|\psi\rangle = \sum_n c_n|n\rangle$.

From discrete to continuous, summation becomes integral.

Similarly, for continuous $x$, an arbitrary state $|\psi\rangle = \int_{-\infty}^{\infty} dx\, \psi(x)\, |x\rangle$.

The amplitude becomes a continuous function.

$c_0 = \langle 0|\chi\rangle$ and $c_1 = \langle 1|\chi\rangle$ $\quad$ $c_n = \langle n|\psi\rangle$ $\quad$ by analogy $\quad$ $\psi(x) = \langle x|\psi\rangle$

discrete

For continuous $x$

$|\chi\rangle = \begin{pmatrix} c_0 \\ c_0 \end{pmatrix}$

How do you write $|\psi\rangle$ as a 1-column, N-dimensional matrix?

For the continuous case, we don't have a way to do that.

Here, for continuous $x$, $\psi(x)$ is the amplitude of $|x\rangle$ in $|\psi\rangle$, i.e., projection of $|\psi\rangle$ onto $|x\rangle$, just as $c_n$ is to $|\psi\rangle = \sum_n c_n|n\rangle$ in the discrete case.

**Question:** What is the physical meaning of $|\psi(x)|^2$?

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**Answer:** Just as $|c_n|^2 = |\langle n|\chi\rangle|^2$ is the probability of finding the system in state $|n\rangle$, $|\psi(x)|^2 dx = |\langle x|\psi\rangle|^2 dx$ is the probability of finding the particle in state $|x\rangle$, i.e., at location $x$ within a neighbood $dx$ long..

You may have learned that $\psi(x)$ is the wave function.

As amplitudes of discrete states, the wave function is to be normalized.

$$\sum_n |c_n|^2 = \sum_n |\langle n|\chi\rangle|^2 = 1 \qquad \int_{-\infty}^{\infty} dx |\langle x|\psi\rangle|^2 = \int_{-\infty}^{\infty} dx |\psi(x)|^2 = 1$$

**Note:** Not all wave functions can be normalized this way. We will re-examine normalization later.

$\psi(x) \equiv \langle x|\psi\rangle$ is the wave function.
$|\psi(x)|^2$ is the probability density,

**Question:**
What is the unit of $\psi(x)$ in 1D space?

If we can write down the H of a (1-particle) system, we can find the stationary states $|n\rangle$ and eigenvalues $E_n$.
We can then trace the time evolution of any arbitrary state $|\psi(t)\rangle = \sum_n c_n(t)|n(t)\rangle$.
For any stationary state $|n\rangle$, we can find its wave function $\psi_n(x) \equiv \langle x|n\rangle$, and then we know the probability distribution of the particle in space.
We can also find the wave function of an arbitrary state $\psi(x) \equiv \langle x|\psi\rangle$.
Thus we know everything about the system that we ***can*** know.

Therefore, it is critical to know H.

Recall the following:

> Relations between operators in quantum mechanics follow those between the corresponding physical quantities known in classical physics.

The Hamiltonian operator $\mathrm{H} = \frac{\mathrm{p}^2}{2m} + V(x)$

Momentum operator

Potential ***energy***

Mass

**Side note**: Here, in 1D, momentum $p$ is considered a scalar.

To know H, we need to know p.

Next, we introduce the Schrödinger equation in the wave function form without rigorous proof (to be given later).

Let $|p\rangle$ be an momentum eigenstate with eigenvalue $p$, we can then write:

$$\mathrm{p}|p\rangle = p|p\rangle$$

momentum eigenvalue

momentum operator

momentum eigenstate corresponding to eigenvalue $p$

$\mathrm{p}|p\rangle = p|p\rangle \Rightarrow \langle x|\mathrm{p}|p\rangle = p\langle x|p\rangle \Rightarrow \mathrm{p}\langle x|p\rangle = p\langle x|p\rangle$

This step will be discussed later.

Inserting the wave function of the momentum eigenstate $\langle x|p\rangle \equiv \psi_p(x)$, we get:

$$\mathrm{p}\,\psi_p(x) = p\,\psi_p(x) \qquad (1)$$

Here, operator p acts on wave function $\psi_p(x)$.

You may have learned that the momentum eigenstate is a plane wave, that is,

$$\psi_p(x) = e^{ikx}$$

$$k = p/\hbar$$

**Side note**: With time evolution included, $\langle x|p(t)\rangle = \psi_p(x,t) = e^{ikx-i\omega t}$

Right side of Eq. (1): $p\,\psi_p(x) = k\hbar e^{ikx}$

Noticing $\frac{d}{dx}e^{ikx} = ike^{ikx}$, we immediately see

$$p\,\psi_p(x) = k\hbar e^{ikx} = \frac{\hbar}{i}\left(ike^{ikx}\right) = -i\hbar\frac{d}{dx}e^{ikx}.$$

Compare this to the left side of Eq. (1), we find

$$\mathrm{p} = -i\hbar\frac{d}{dx}$$

This is the form of momentum operator p when acting on a wave function.

$$\mathrm{p} = -i\hbar\frac{d}{dx}$$

insert

$$\mathrm{H} = \frac{\mathrm{p}^2}{2m} + V(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

This means the Schrödinger equation can be solved as follows:

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

There are stationary solutions: $|\psi_n(t)\rangle = e^{-i\frac{E_n}{\hbar}t}|n\rangle$ $\qquad \mathrm{H}|n\rangle = E_n|n\rangle$

$$\psi_n(x,t) \equiv \langle x|\psi_n(t)\rangle = e^{-i\frac{E_n}{\hbar}t}\langle x|n\rangle \qquad \langle x|\mathrm{H}|n\rangle = E_n\langle x|n\rangle$$

insert

$$\psi_n(x) \equiv \langle x|n\rangle$$

$$\psi_n(x,t) = e^{-i\frac{E_n}{\hbar}t}\psi_n(x) \qquad \mathrm{H}\psi_n(x) = E_n\psi_n(x)$$

We usually write the Schrödinger equation in the wave function form as

$$i\hbar\frac{d}{dt}\psi(x,t) = \mathrm{H}\psi(x,t)$$

$$\mathrm{H}\psi(x) = E\psi(x)$$

We usually write the Schrödinger equation in the wave function form as

$$i\hbar\frac{d}{dt}\psi(x,t) = \mathrm{H}\psi(x,t) \qquad \mathrm{H}\psi(x) = E\psi(x)$$

Then, insert $\mathrm{H} = \frac{\mathrm{p}^2}{2m} + V(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$

$$i\hbar\frac{d}{dt}\psi(x,t) = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi \qquad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x)$$

or

$$i\hbar\frac{d}{dt}\psi(x,t) = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x,t) \qquad \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x)$$

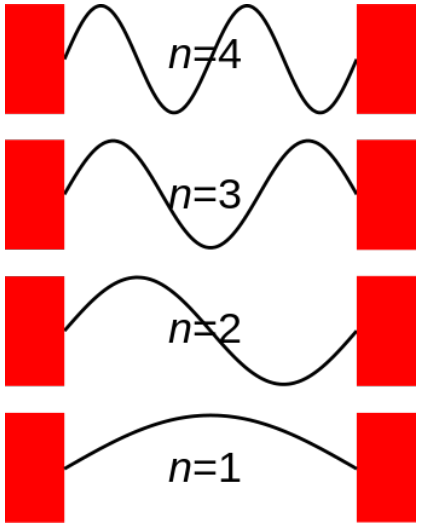
(Stationary state Schrödinger equation)

This is the starting point of the conventional way to teach quantum mechanics.
Lots of examples will be solved for various potentials and boundary conditions.

# Important examples

**Example 1**: One-dimensional infinitely deep well

$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)$ inside the well $(0 < x < a)$, $\psi(x) = 0$ outside.




https://en.wikipedia.org/wiki/Particle_in_a_box

Discussions:

1D standing wave, like that of a string or a transmission line with both ends shorted.

We usually label the ground state in such a potential well with $n = 1$.

$$E_n \propto n^2, E_n \propto 1/a^2.$$

States with even and odd symmetry.

Do H and p have simultaneous eigenstates? What are the eigenstates of p?

The concept of "good" quantum numbers.

**Example 2**: Three-dimensional hard-wall box

$\mathrm{p} = -i\hbar\frac{d}{dx}$ → Extend to 3D → $\mathbf{p} = -i\hbar\boldsymbol{\nabla}$

Vector operator per our notation

Discussions: Quantum numbers $n_x$, $n_y$, $n_z$; accidental degeneracy (3 edges may be different).

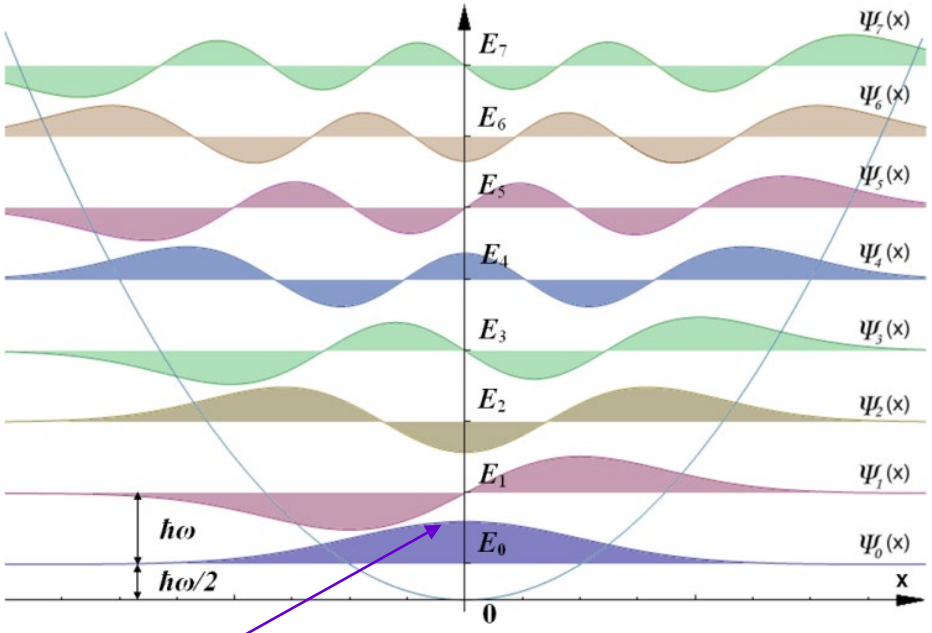
**Example 3**: One-dimensional harmonic oscillator

$$V(x) = \frac{1}{2}Kx^2 = \frac{1}{2}m{\omega_0}^2x^2$$

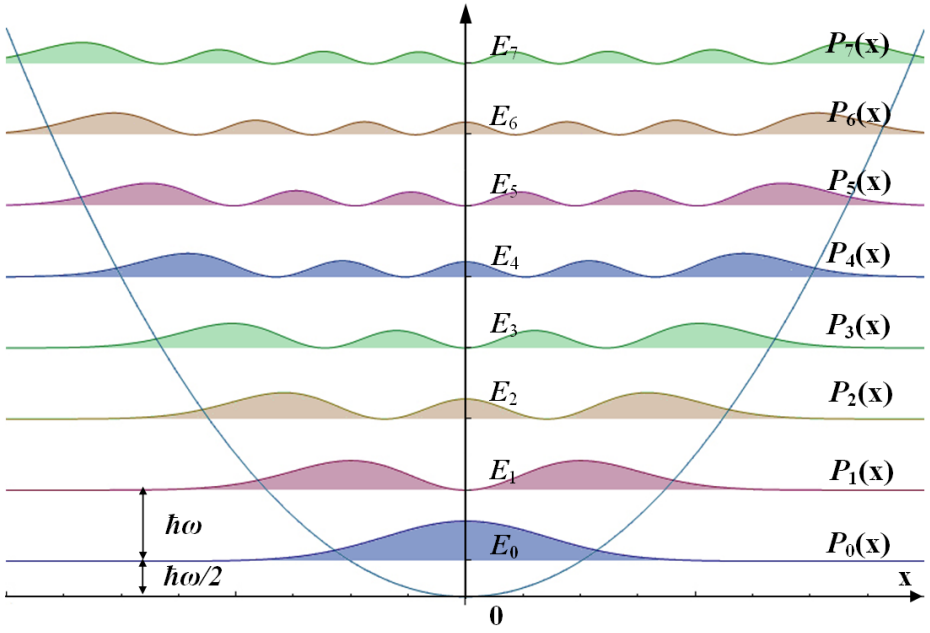
$$\omega_0 = \sqrt{\frac{K}{m}} \Rightarrow K = m{\omega_0}^2$$

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_0$$

Wave functions




Probability distributions




$\psi_0(x) = e^{-\frac{m\omega_0}{2\hbar}x^2}$

Figures from Wikipedia page https://en.wikipedia.org/wiki/Quantum_harmonic_oscillator.

Discussions: Energy intervals; zero point energy; symmetry; regions where $E_n < V(x)$.

What is $\psi_0(x,t)$? What is $\psi_n(x,t)$, given stationary $\psi_n(x)$?

Watch animation at Wikipedia page
https://en.wikipedia.org/wiki/Quantum_harmonic_oscillator

**Example 4**: One-dimensional finite-depth well

Discussions: Energy intervals; symmetry; regions where $E_n < V(x)$.
Wave function tails and tunneling. Consider two wells close to each other.

Choice of setting the zero reference for energy: for your convenience.

As for the hard-wall cases, we can also have cases where the particle is free in on or two dimensions. EM wave analogy: dielectric cavities and waveguides. Notice the differences. (For future discussion; quantum well devices)

**Example 5**: H atom

$V(\mathbf{r}) = -\dfrac{e^2}{4\pi\varepsilon_0 r}$. $V(\infty) = 0$. Central force: angular momentum $\boldsymbol{L}$ conserved.

Recall that for spin, H, $\mathbf{S}^2$, and $S_z$ have simultaneous eigenstates, but $S_x$, $S_y$, and $S_z$ do not. Similarly for orbital motion, H, $\mathbf{L}^2$, and $L_z$ have simultaneous eigenstates, but $L_x$, $L_y$, and $L_z$ do not.

For spin, $S^2 = s(s+1)\hbar^2$, where $s$ = ½ thus $S^2 = \frac{3}{4}\hbar^2$, and $S_z = m_s\hbar$, where $m_s = \pm\frac{1}{2}$; $s$ and $m_s$ are spin angular momentum quantum numbers. (Here, $s$ is not the dimensionless quantity $S/(\hbar/2)$ we defined in **Part 1**. $m_s = s_z$.)
For orbital motion, $L^2 = l(l+1)\hbar^2$, where $l$ = 0, 1, 2, …, and $L_z = m\hbar$, where $m = 0, \pm1, \pm2$, …, $\pm l$, ($|m| \le l$): $l$ and $m$ are orbital angular momentum quantum numbers.

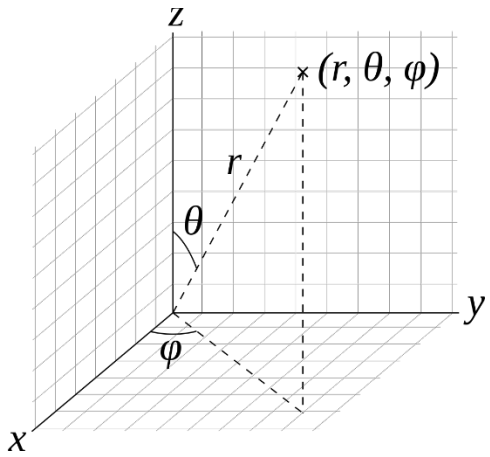
Choose spherical coordinate system ($r$, $\theta$, $\varphi$). Get radial and angular equations.

Choose spherical coordinate system $(r, \theta, \varphi)$. Get radial and angular equations by variable separation.

The solutions are $\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi)$, where the spherical harmonics $Y_{lm}$ are solutions to angular momentum eigenvalue equations

$$\boldsymbol{L}^2 Y_{lm}(\theta,\varphi) = l(l+1)\hbar^2 Y_{lm}(\theta,\varphi), \qquad \boldsymbol{L}_z Y_{lm}(\theta,\varphi) = m\hbar Y_{lm}(\theta,\varphi)$$

$l$ are non-negative integers; $|m| \le l$




Further separate $\theta$ and $\varphi$: $Y_{lm}(\theta,\varphi) = \Theta_{lm}(\theta)\frac{1}{\sqrt{2\pi}}e^{im\varphi}$

Real valued

Normalization with regard to $\varphi$

Normalization

$$\int_0^{\pi} d\theta(\sin\theta)\int_0^{2\pi} d\varphi |Y_{lm}(\theta,\varphi)|^2 = 1$$

$$\int_0^{2\pi} d\varphi \left|\frac{1}{\sqrt{2\pi}}e^{im\varphi}\right|^2 = 1$$

$$\Rightarrow \int_0^{\pi} d\theta |\Theta_{lm}(\theta)|^2 \sin\theta = 1$$

$l = 0, m = 0$: *s* orbital. $Y_{00}(\theta,\varphi) = \frac{1}{\sqrt{4\pi}}$

An orbital is a single-electron state.

Solid angle of entire 3D space is $4\pi$.

Normalization $\frac{1}{2}\int_0^{\pi} d\theta \sin\theta = 1$

Angular momentum eigenvalues $L^2 = 0$, $L_z = 0$.

$l = 1, m = 0, \pm 1$: $p$ orbitals

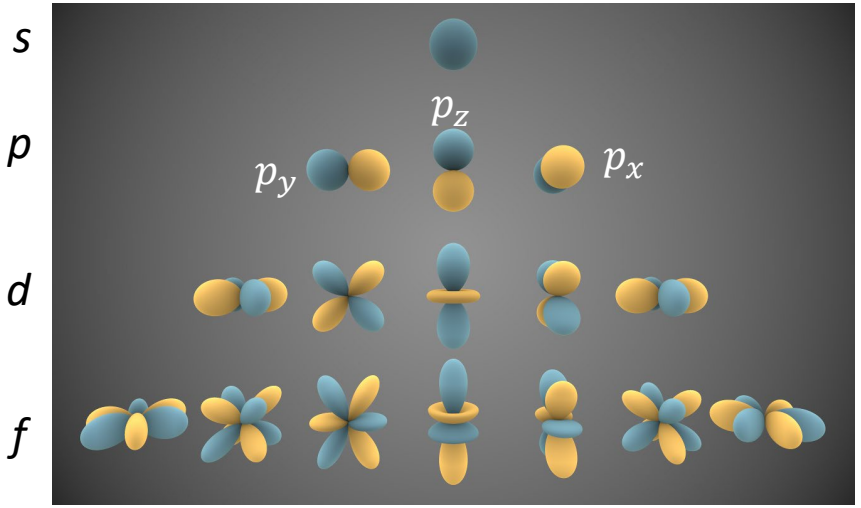
$l = 1, m = 0$: $p_z$ orbital,
eigenvalues $L^2 = 2\hbar^2$, $L_z = 0$.

$|Y_{10}(\theta, \varphi)|^2$

http://mathworld.wolfram.com/SphericalHarmonic.html

$$Y_{10}(\theta, \varphi) = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$\Theta_{10}(\theta) = \sqrt{\frac{3}{2}} \cos\theta \Rightarrow \frac{3}{2} \int_0^{\pi} d\theta \cos^2\theta \sin\theta = 1$$




https://en.wikipedia.org/wiki/Spherical_harmonics

$l = 1, m = \pm 1$: linear combinations form **real-valued** $p_x$ and $p_y$ orbitals (which are ***not*** eigenstates of $L_z$), angular momentum eigenvalues $L^2 = 2\hbar^2$, $L_z = \pm\hbar$.

$|Y_{10}(\theta, \varphi)|^2$  

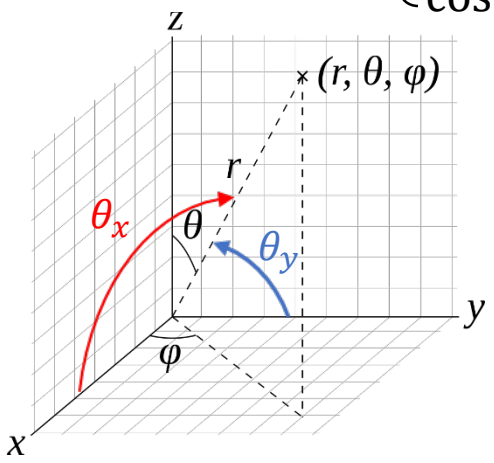
$$Y_{1,\pm 1}(\theta, \varphi) = \mp\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{\pm i\varphi}$$

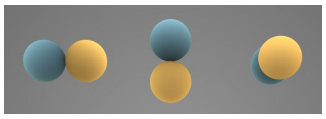
http://mathworld.wolfram.com/SphericalHarmonic.html

$$\Rightarrow \begin{cases} \frac{i}{\sqrt{2}}\left(Y_{1,-1} + Y_{1,-1}\right) = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\varphi & p_y \\ \frac{1}{\sqrt{2}}\left(Y_{1,-1} - Y_{1,-1}\right) = \sqrt{\frac{3}{4\pi}} \sin\theta \cos\varphi & p_x \end{cases}$$

You define polar angle from $y$ axis, $\theta_y$,
and polar angle from $x$ axis, $\theta_x$.

Easy to show $\begin{cases} \cos\theta_y = \sin\theta\sin\varphi \\ \cos\theta_x = \sin\theta\cos\varphi \end{cases}$

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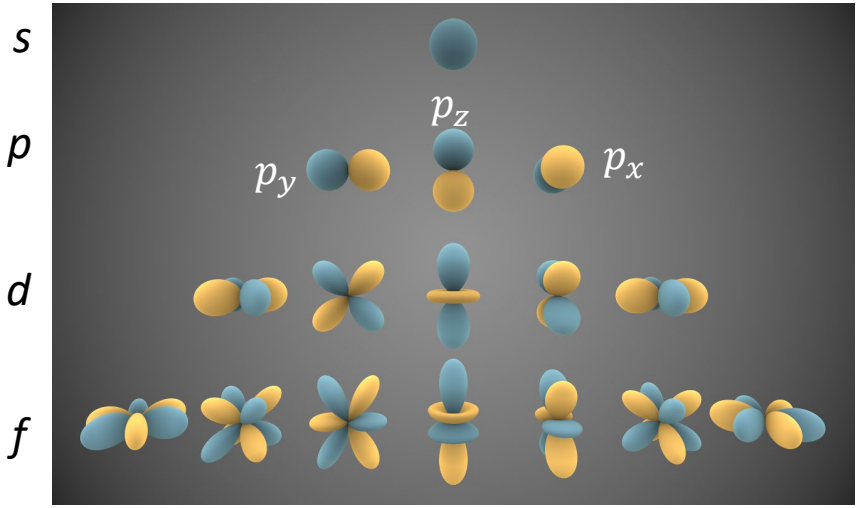


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$$\begin{cases} \frac{i}{\sqrt{2}}\left(Y_{1,-1}+Y_{1,1}\right) = \sqrt{\frac{3}{4\pi}}\sin\theta\sin\varphi = \sqrt{\frac{3}{4\pi}}\cos\theta_y & p_y \\ \frac{1}{\sqrt{2}}\left(Y_{1,-1}-Y_{1,1}\right) = \sqrt{\frac{3}{4\pi}}\sin\theta\cos\varphi = \sqrt{\frac{3}{4\pi}}\cos\theta_x & p_x \end{cases}$$

Compare: $Y_{10}(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\theta$ $\quad p_z$

Interesting to note that
$p_z$ is the eigenstate with $L^2 = 2\hbar^2$, $L_z = 0$ ($l = 1$, $m \equiv m_z = 0$);
$p_y$ is the eigenstate with $L^2 = 2\hbar^2$, $L_y = 0$ ($l = 1$, $m_y = 0$);
$p_x$ is the eigenstate with $L^2 = 2\hbar^2$, $L_x = 0$ ($l = 1$, $m_x = 0$).

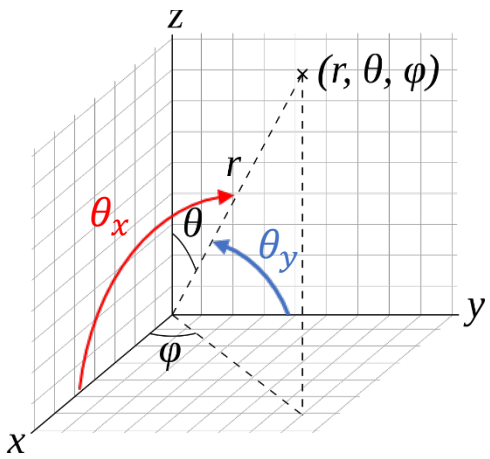
**FYI**: $p_x, p_y, p_z$ orbitals and spherical harmonics

The $p_x, p_y, p_z$ orbitals are real-valued. (Overall phase of one state irrelevant; the three are in phase.)

$$p_z = Y_{10}(\theta, \varphi) = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$\left.\begin{aligned} p_y &= \frac{i}{\sqrt{2}}\left(Y_{1,-1} + Y_{1,1}\right) = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\varphi = \sqrt{\frac{3}{4\pi}} \cos\theta_y \\ p_x &= \frac{1}{\sqrt{2}}\left(Y_{1,-1} - Y_{1,1}\right) = \sqrt{\frac{3}{4\pi}} \sin\theta \cos\varphi = \sqrt{\frac{3}{4\pi}} \cos\theta_x \end{aligned}\right\}$$

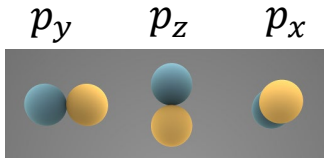
$$\Rightarrow \begin{cases} Y_{1,1} = \dfrac{p_x + i p_y}{\sqrt{2}} \\ Y_{1,-1} = \dfrac{p_x - i p_y}{\sqrt{2}} \end{cases}$$




Define polar angle from $y$ axis, $\theta_y$, and polar angle from $x$ axis, $\theta_x$.

$$\cos\theta_y = \sin\theta \sin\varphi$$

$$\cos\theta_x = \sin\theta \cos\varphi$$

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$p_z$ is the eigenstate with $L^2 = 2\hbar^2$, $L_z = 0$ ($l = 1$, $m \equiv m_z = 0$);
$p_y$ is the eigenstate with $L^2 = 2\hbar^2$, $L_y = 0$ ($l = 1$, $m_y = 0$);
$p_x$ is the eigenstate with $L^2 = 2\hbar^2$, $L_x = 0$ ($l = 1$, $m_x = 0$).

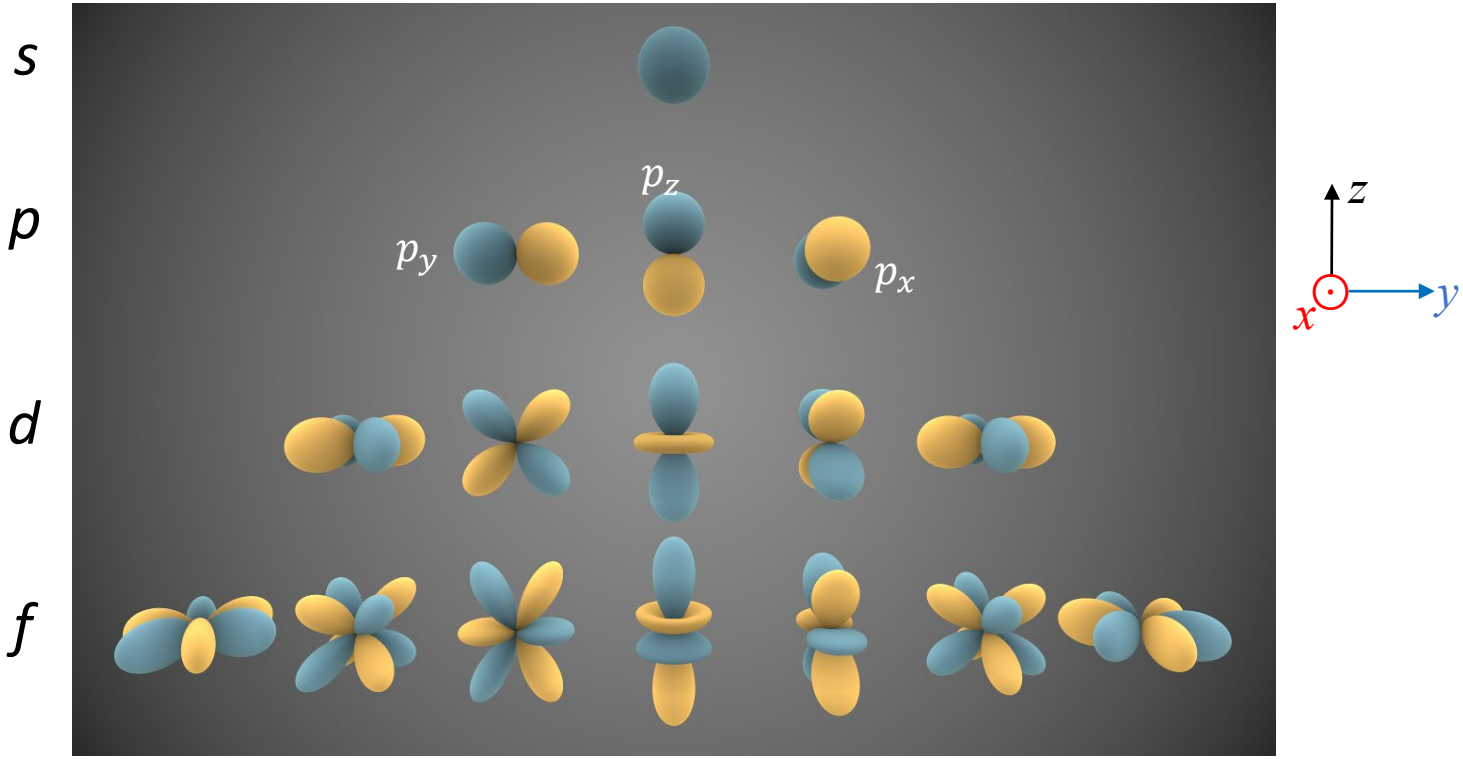
$l = 2$, $m = 0, \pm 1, \pm 2$: Five *d* orbitals

Angular momentum eigenvalues $L^2 = 6\hbar^2$.

For $m \neq 0$, linear combinations of $Y_{2,m}$ form **real-valued** *d* orbitals.

$l = 3$, $m = 0, \pm 1, \pm 2, \pm 3$: seven *f* orbitals

Angular momentum eigenvalues $L^2 = 12\hbar^2$.




https://en.wikipedia.org/wiki/Spherical_harmonics

These are solutions to the angular equation, which is the angular momentum eigenvalue equation.

The overall solutions are $\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi)$.

For all central forces, the angular solutions $Y_{lm}(\theta,\varphi)$ are the same.

For a general central force, the radial solutions $R_{nl}(r)$ correspond to energy eigenvalues $E_{nl}$.

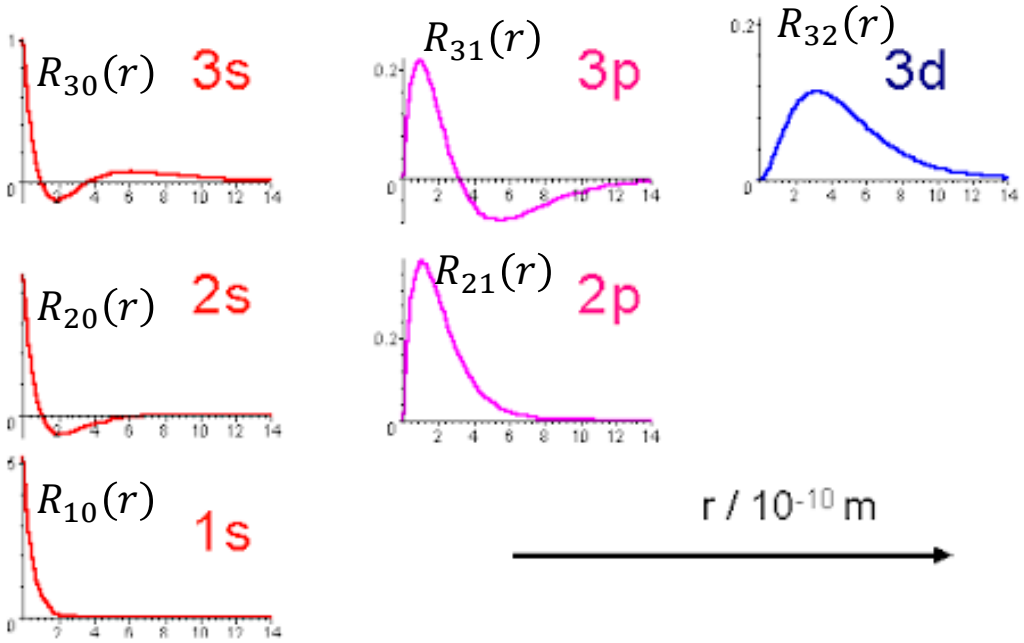
For the Coulomb force of ***a point charge***, energy eigenvalues $E_{nl}$ is degenerate for all $l$, thus simply $E_n$ (but $R_{nl}(r)$ are still different for different $l$). H-like ions e.g. $He^+$

$n = 1, 2, 3, \ldots$

$l = 0, 1, 2, \ldots, n-1$

$$E_n = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{me^4}{2\hbar^2}\frac{1}{n^2}$$

**Electron wave functions of atomic hydrogen $R_{nl}(r)$**

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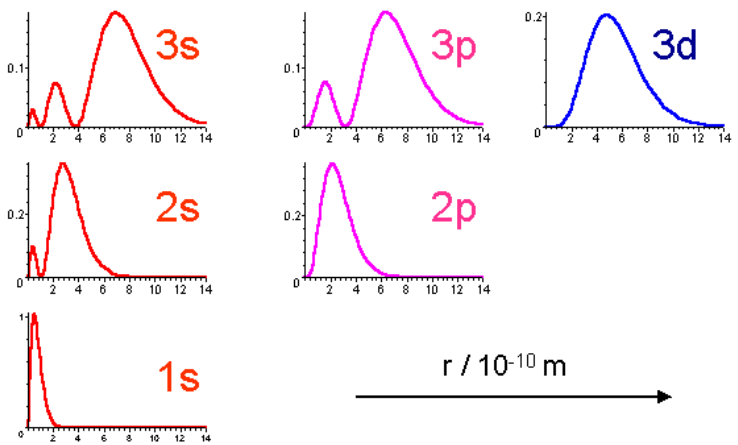
$|rR_{nl}(r)|^2$

**Electron density in atomic hydrogen w(r) = r² [$R_{nl}$(r)]²**

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Our discussion paused here on Thu 2/9/2023.

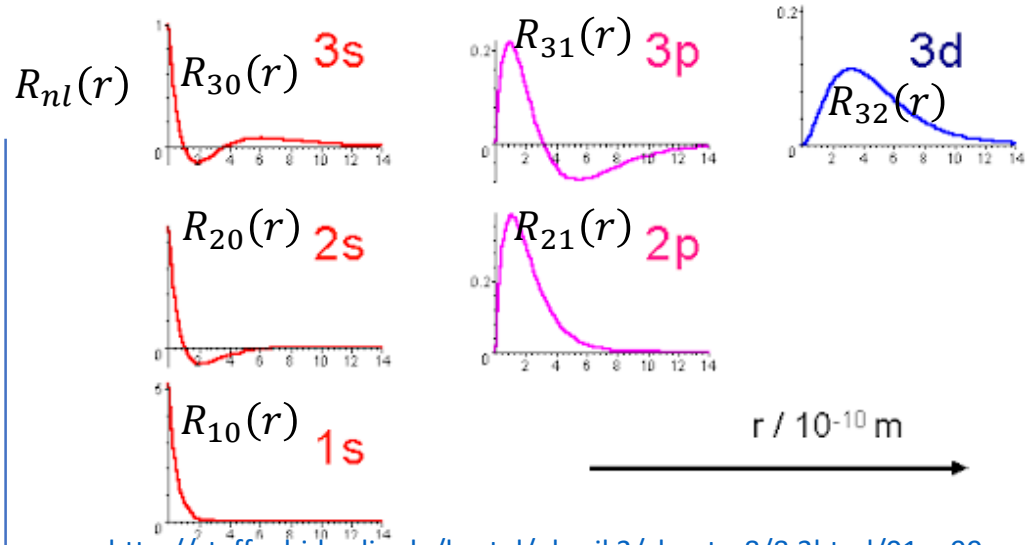
Visualization of $R_{nl}(r)$

$n = 1, 2, 3, \ldots$

$l = 0, 1, 2, \ldots, n-1$

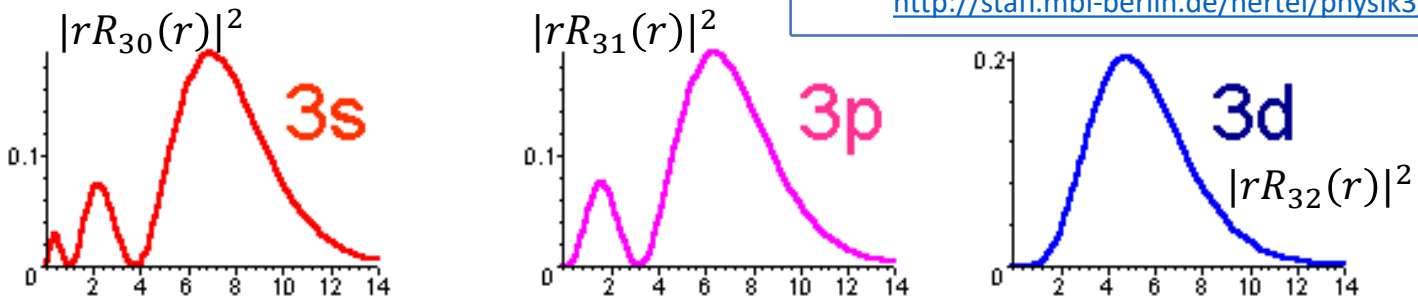
Bohr radius $a_0 = 4\pi\varepsilon_0 \frac{\hbar^2}{me^2}$

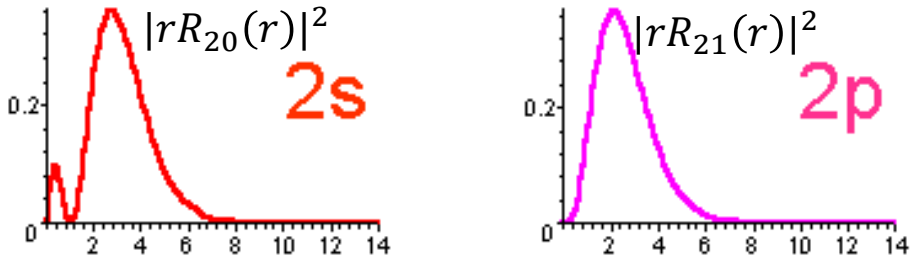
$$E_n = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{me^4}{2\hbar^2}\frac{1}{n^2} = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{2a_0}\frac{1}{n^2}$$




http://staff.mbi-berlin.de/hertel/physik3/chapter8/8.3html/01__99.png

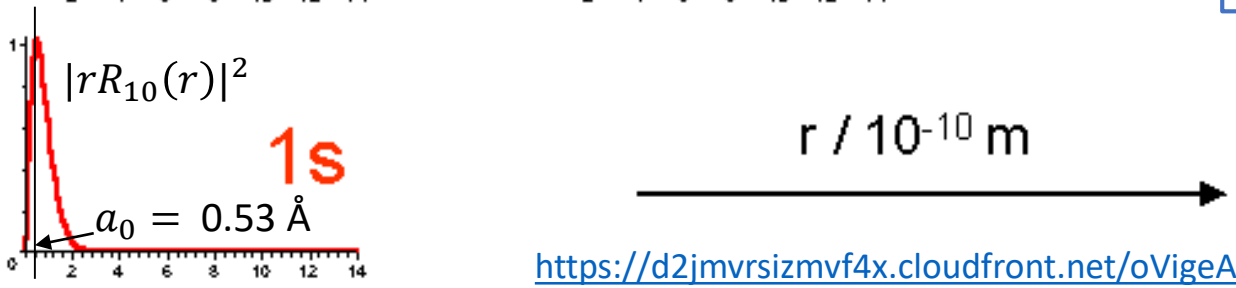
$|rR_{nl}(r)|^2$



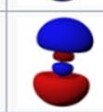
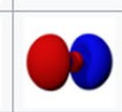
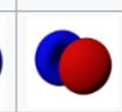
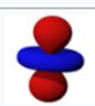
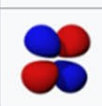
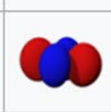
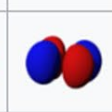
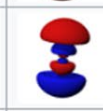
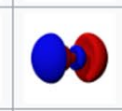
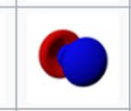
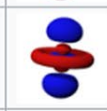
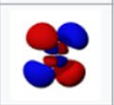
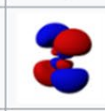
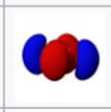
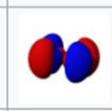
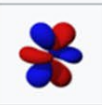
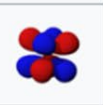
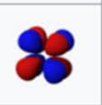
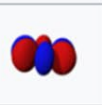
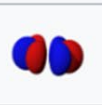
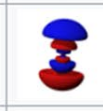
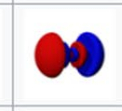
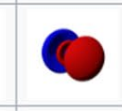
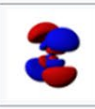
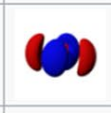
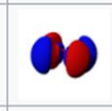

$E_1 = -13.6$ eV

$a_0 = 0.53$ Å

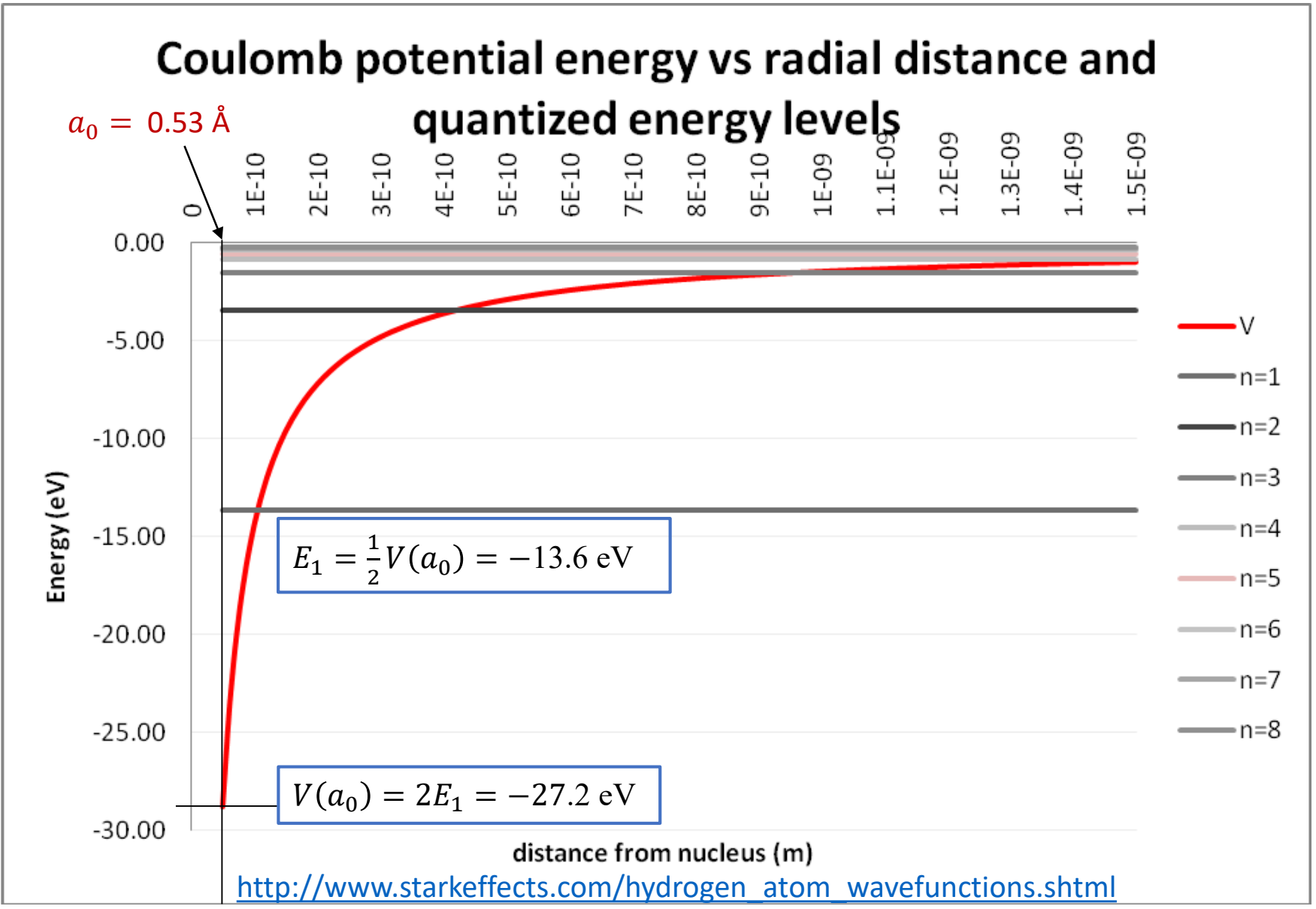



https://d2jmvrsizmvf4x.cloudfront.net/oVigeAgPQwC2STwkBOQr_01__100.png

Visualization of the overall wave functions $\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi)$

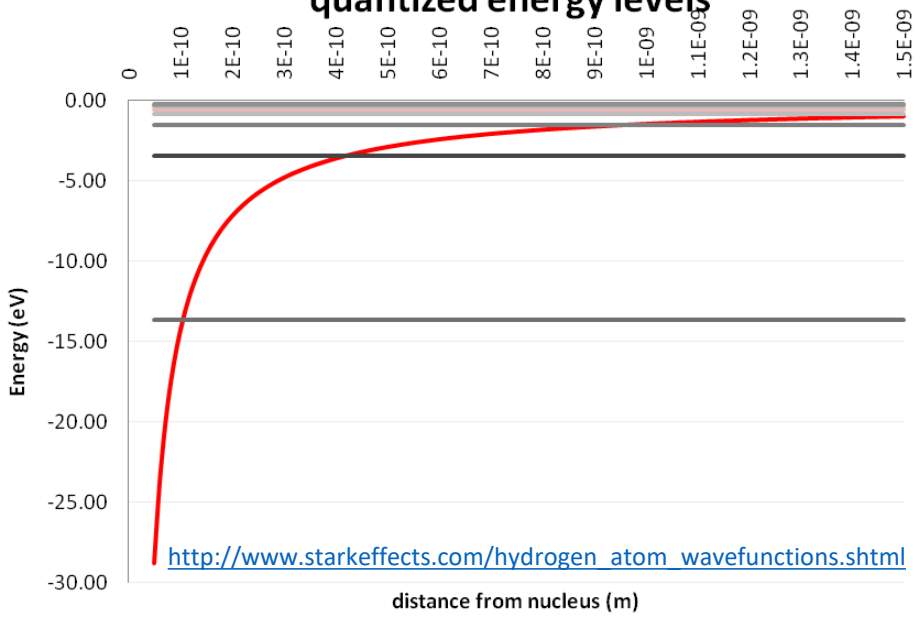
| | s ($\ell = 0$) | p ($\ell = 1$) | | | d ($\ell = 2$) | | | | | f ($\ell = 3$) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $m = 0$ | $m = 0$ | $m = \pm 1$ | | $m = 0$ | $m = \pm 1$ | | $m = \pm 2$ | | $m = 0$ | $m = \pm 1$ | | $m = \pm 2$ | | $m = \pm 3$ | |
| | s | $p_z$ | $p_x$ | $p_y$ | $d_{z^2}$ | $d_{xz}$ | $d_{yz}$ | $d_{xy}$ | $d_{x^2-y^2}$ | $f_{z^3}$ | $f_{xz^2}$ | $f_{yz^2}$ | $f_{xyz}$ | $f_{z(x^2-y^2)}$ | $f_{x(x^2-3y^2)}$ | $f_{y(3x^2-y^2)}$ |
| $n = 1$ |  | | | | | | | | | | | | | | | |
| $n = 2$ |  |  |  |  | | | | | | | | | | | | |
| $n = 3$ |  |  |  |  |  |  |  |  |  | | | | | | | |
| $n = 4$ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| $n = 5$ |  |  |  |  |  |  |  |  |  | … | … | … | … | … | … | … |
| $n = 6$ |  |  |  |  | … | … | … | … | … | … | … | … | … | … | … | … |

https://en.wikipedia.org/wiki/Atomic_orbital



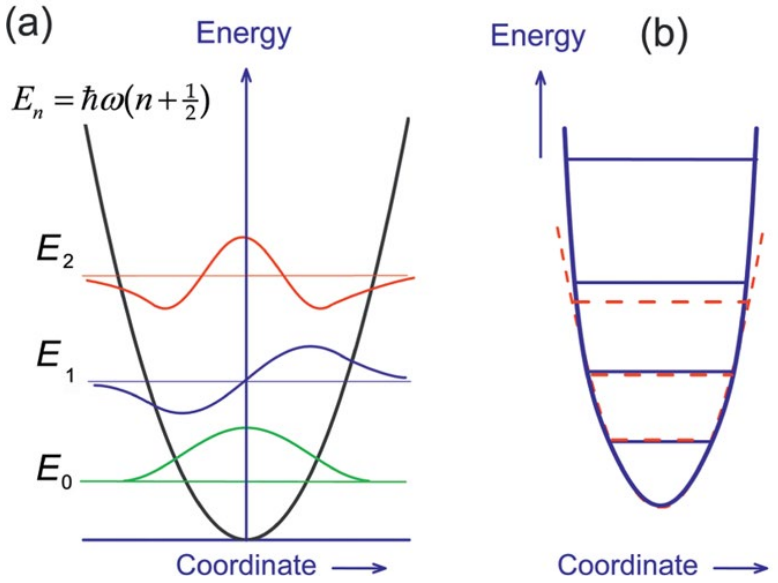

http://www.starkeffects.com/hydrogen_atom_wavefunctions.shtml

## Coulomb potential energy vs radial distance and quantized energy levels

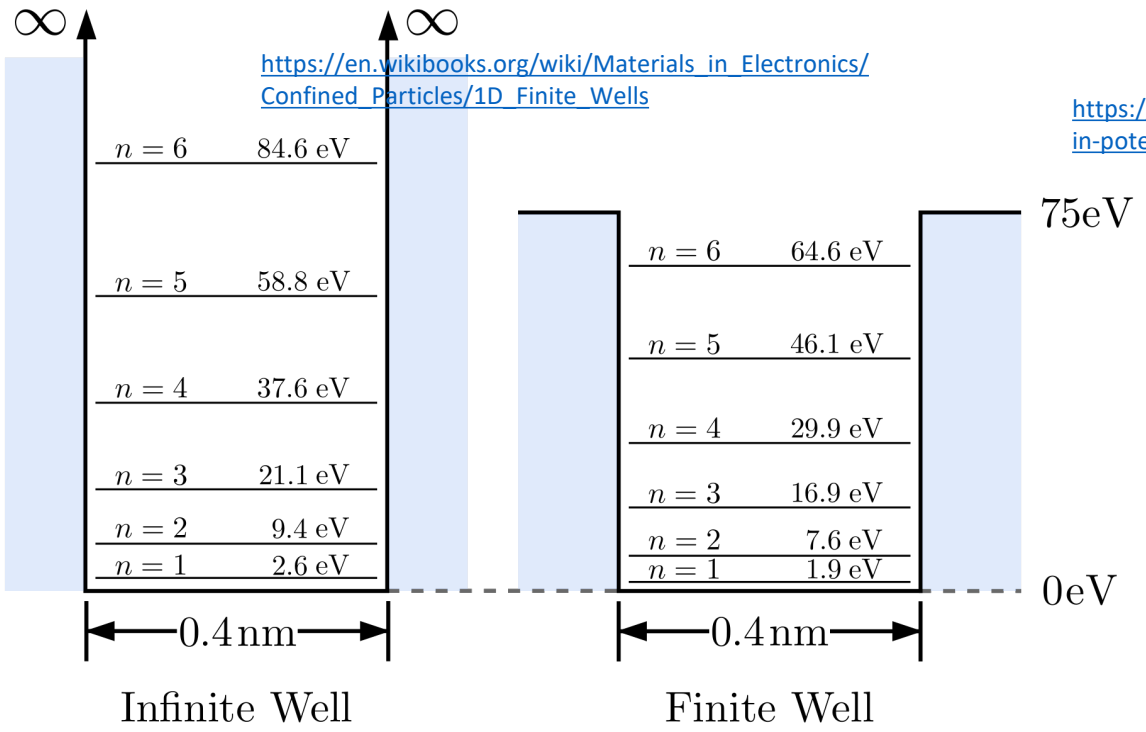



http://www.starkeffects.com/hydrogen_atom_wavefunctions.shtml

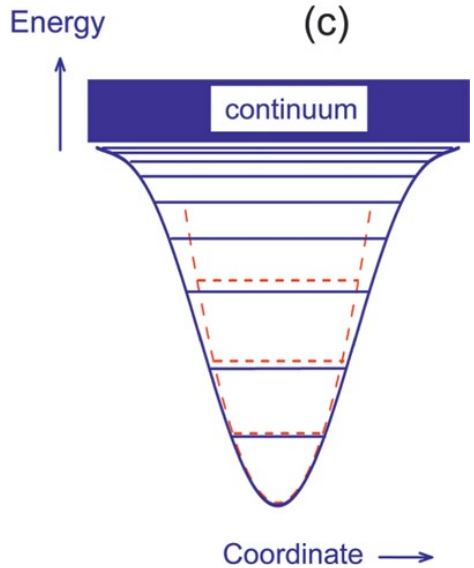
## Potential well shapes and energy level distributions




https://www.cambridge.org/core/books/applied-nanophotonics/electrons-in-potential-wells-and-in-solids/D1A1D672320B55539DE286196D51EF47




https://en.wikibooks.org/wiki/Materials_in_Electronics/Confined_Particles/1D_Finite_Wells

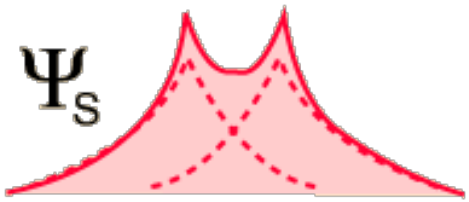


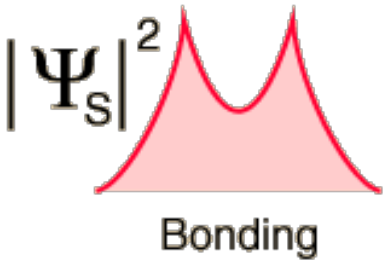
**Example 5**: $H_2^+$

With the two protons fixed at a constant distance, the $H_2^+$ is an analytically solvable 1-e problem.

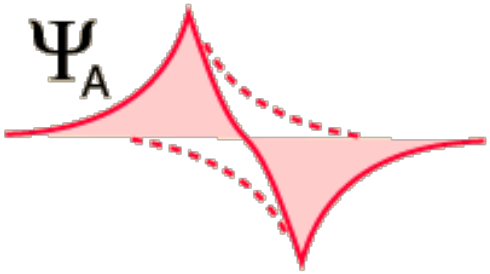
We focus on the two lowest stationary states: ground state $|0\rangle$ and first excited state $|1\rangle$ .

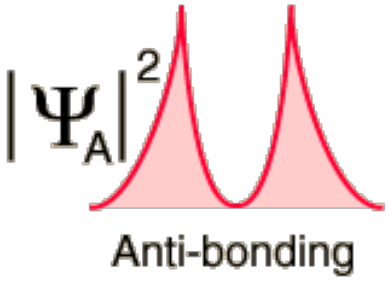
$\psi_S(\boldsymbol{r}) = \langle \boldsymbol{r}|0\rangle$ Symmetric

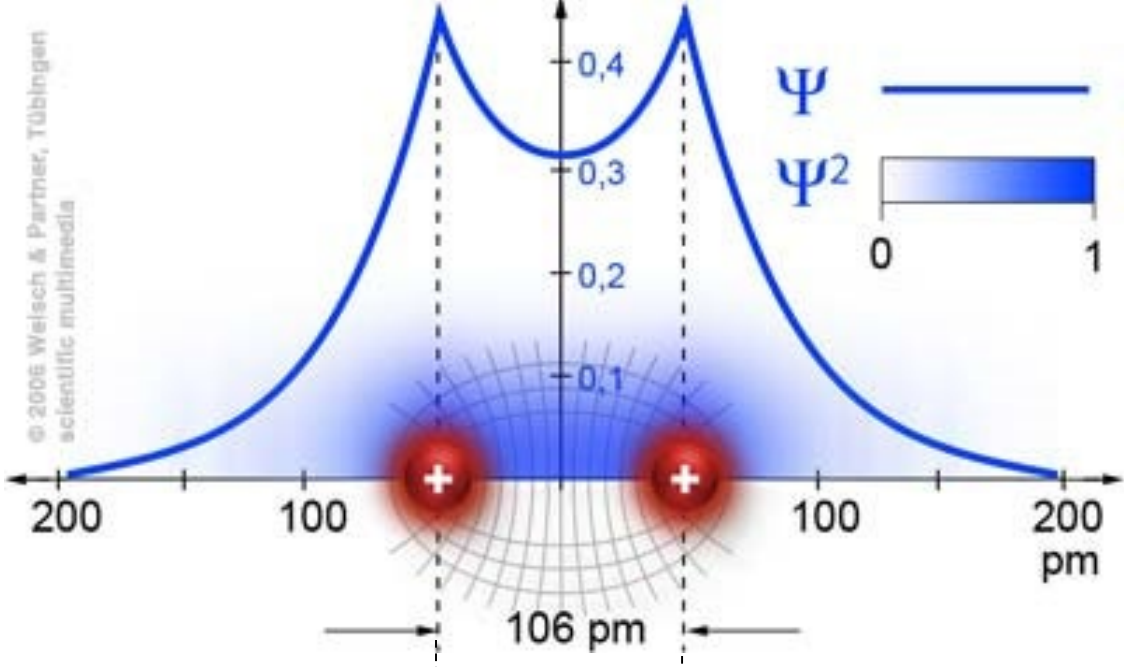


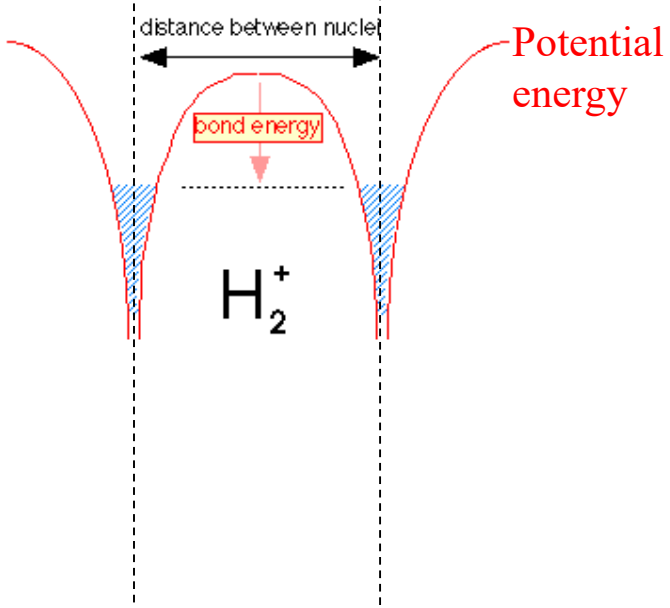




$\psi_A(\boldsymbol{r}) = \langle \boldsymbol{r}|0\rangle$ Antisymmetric



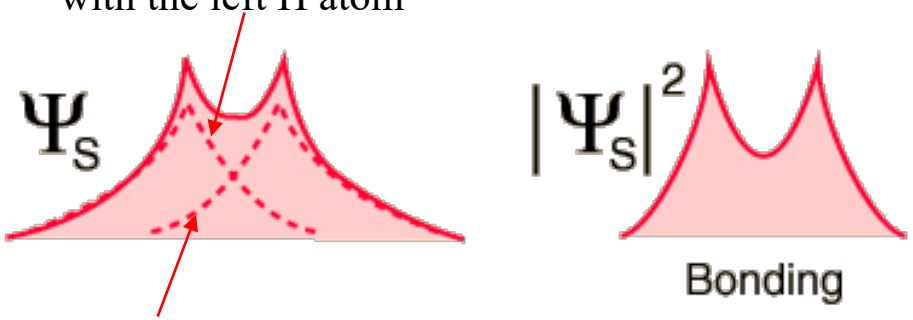
## $H_2^+$ is a 2-state system

We ***view*** the electron as shared by the two protons, resulting in two stationary states:

Bonding: $|0\rangle = \frac{1}{\sqrt{2}}(|L\rangle + |R\rangle)$ and

Antibonding: $|1\rangle = \frac{1}{\sqrt{2}}(|L\rangle - |R\rangle)$

$\phi_L(\boldsymbol{r}) = \langle \boldsymbol{r}|L\rangle$: the electron "associated" with the left H atom




$\phi_R(\boldsymbol{r}) = \langle \boldsymbol{r}|R\rangle$: the electron "associated" with the right H atom


Here, $|L\rangle$ and $|R\rangle$ are ***not*** the H 1s atomic orbitals.
Rather, they are found ***after*** the stationary states are found:

$$|L\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) \text{ and}$$
$$|R\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle)$$

$$\langle L|L\rangle = \langle R|R\rangle = 1,$$
$$\langle L|R\rangle = \langle R|L\rangle = 0$$

# $H_2^+$ is a 2-state system

Bonding: $|0\rangle = \frac{1}{\sqrt{2}}(|L\rangle + |R\rangle)$ and

Antibonding: $|1\rangle = \frac{1}{\sqrt{2}}(|L\rangle - |R\rangle)$

$|L\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)$ and

$|R\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle)$

## Questions:

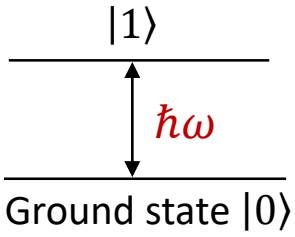
If we prepare an $H_2^+$ in an initial state $|L\rangle$ at $t = 0$ and "measure" whether the electron is associated with the left or right proton, how do the probabilities of finding it associated with the left and right protons change with time?

What if we prepare the $H_2^+$ in $|0\rangle$ at $t = 0$ ?

Hint: Use spin analogy.

## Answers:

If we prepare an $H_2^+$ in $|L\rangle$ at $t = 0$ and measure whether the electron is associated with the left or right proton, the probabilities of finding left and right will oscillate back and forth at the frequency determined by the energy difference between the bonding ($|0\rangle$) and antibonding ($|1\rangle$) states.

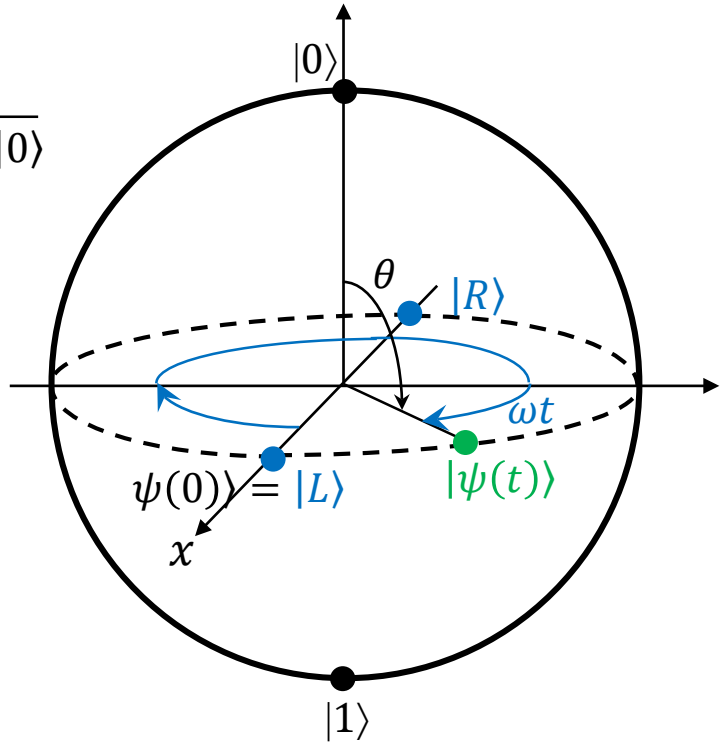



$$|\psi(t)\rangle = \left(\cos\frac{\omega}{2}t\right)|L\rangle + \left(\sin\frac{\omega}{2}t\right)|R\rangle.$$

The probabilities are

$\cos^2\frac{\omega}{2}t = \frac{1}{2}(1 + \cos\omega t)$ left,

$\sin^2\frac{\omega}{2}t = \frac{1}{2}(1 - \cos\omega t)$ right.




If we prepare the $H_2^+$ in $|0\rangle$ at $t = 0$, it will stay there forever since $|0\rangle$ is stationary. The probabilities are half/half for finding it left and right.

# Re-examine the wave function form of Schrödinger equation

From previous slides:

Momentum operator

Potential ***energy***

The Hamiltonian operator $\mathrm{H} = \frac{\mathrm{p}^2}{2m} + V(x)$

Mass

**Side note**: Here, in 1D, momentum $p$ is considered a scalar.

To know H, we need to know p.

Next, we introduce the Schrödinger equation in the wave function form without rigorous proof (to be given later).

Let $|p\rangle$ be an momentum eigenstate with eigenvalue $p$, we can then write:

momentum operator

momentum eigenvalue

$$\mathrm{p}|p\rangle = p|p\rangle \Rightarrow \langle x|\mathrm{p}|p\rangle = p\,\langle x|p\rangle \Rightarrow \mathrm{p}\,\langle x|p\rangle = p\,\langle x|p\rangle$$

momentum eigenstate corresponding to eigenvalue $p$

This step will be discussed later.

Inserting the wave function of the momentum eigenstate $\langle x|p\rangle \equiv \psi_p(x)$, we get:

$$\mathrm{p}\,\psi_p(x) = p\,\psi_p(x) \qquad (1)$$

"Knowing" $\psi_p(x) = e^{ikx}$ with $k = p/\hbar$, we concluded $\boxed{\mathrm{p} = -i\hbar\frac{d}{dx}}$

But, we can't even normalize $\psi_p(x) = e^{ikx}$. Let's have a look back.

The wave function of momentum eigenstate $|p\rangle$ is $\psi_p(x) = \langle x|p\rangle$.

$$\Leftrightarrow \quad |p\rangle = \int_{-\infty}^{\infty} dx\, \psi_p(x)\, |x\rangle$$

Summing up all projections

Let's examine the time evolution of $|p(t)\rangle = \int_{-\infty}^{\infty} dx\, \psi_p(x,t)\, |x\rangle$.

For that, we must look at H.

$$\mathrm{H} = \frac{\mathrm{p}^2}{2m} + V(x) \Rightarrow$$

As long as $V(x) \neq$ constant, H and p do not have common eigenstates.

Why?

$|p\rangle$ is an eigenstate of the H for a ***free particle***: $\mathrm{H} = \frac{\mathrm{p}^2}{2m}$

Therefore, for a ***free particle***, the stationary Schrödinger equation is

Common eigenstate of H and p

$$\mathrm{H}|p\rangle = E(p)|p\rangle = \frac{p^2}{2m}|p\rangle$$

Eigenvalue of H as a function of $p$, which follows the classical relation $E(p) = \frac{p^2}{2m}$.

Since $|p\rangle$ is an eigenstate of H (for a free particle),

$$|p(t)\rangle = e^{-i\frac{E}{\hbar}t}|p(0)\rangle = e^{-i\omega t}\,|p(0)\rangle, \text{ where we define } \omega = E/\hbar.$$

We also define $\langle x|p(t)\rangle = \psi_p(x,t)$ and $\langle x|p(0)\rangle = \psi_p(x,0) = \psi_p(x)$.

Therefore, $\psi_p(x,t) = e^{-i\omega t}\,\psi_p(x,0) = e^{-i\omega t}\,\psi_p(x)$.

$\psi_p(x-vt,0) = \psi_p(x,t)$ since particle classically moves at a constant speed $v = {}^{p}/_{m}$.

$$\Rightarrow \quad \psi_p(x-vt,0) = \psi_p(x-vt) = e^{-i\omega t}\,\psi_p(x).$$

We immediately see $\psi_p(x,t) = c_p e^{-i\omega(t-\frac{x}{v})} = c_p e^{i(\frac{\omega}{v}x-\omega t)}$, where $c_p$ is a constant TBD.

At this point, we have only shown that the momentum eigenstate (of ***a free particle***) is a plane wave, with the phase velocity equal to its classical velocity $v = {}^{p}/_{m}$. Now, let's find the wave vector of this plane wave:

By definition

$$k = \frac{\omega}{v} = \frac{E/\hbar}{{}^{p}/_{m}} = \frac{\frac{p^2}{2m}/\hbar}{{}^{p}/_{m}} = {}^{p}/_{\hbar}$$

($\omega = E/\hbar$ from time evolution)

Therefore, $\psi_p(x,t) = c_p e^{i(kx-\omega t)}$ $\qquad$ $\psi_p(x,0) = \psi_p(x) = c_p e^{ikx}$

$$\psi_p(x,t) = c_p e^{i(kx-\omega t)} \qquad \psi_p(x,0) = \psi_p(x) = c_p e^{ikx}$$

There seems to be an obvious problem: $|\psi_p(x)|^2 = |A|^2$ and thus $\int_{-\infty}^{\infty} dx |\psi_p(x)|^2 = \infty$.

We need to re-examine normalization.

For a physical quantity $Q$ represented by an operator Q, with $N$ ***discrete*** eigenvalues $q_1$, $q_2$, …, $q_n$, …, corresponding to $N$ eigenstates $|q_1\rangle$, $|q_2\rangle$, …, $|q_n\rangle$, …, we have $Q|q_n\rangle = q_n|q_n\rangle$. This can be written in the matrix form.

How?

The state space is $N$-dimensional, and $N$ may be infinity.

The orthonormal condition is formally written as $\langle q_n|q_{n'}\rangle = \delta_{n,n'} \equiv \begin{cases} 0, & n \neq n' \\ 1, & n = n' \end{cases}$.

But, how do we handle situations where the eigenvalue spectrum is continuous?

For eigenstates with a ***discrete*** eigenvalue spectrum, the orthonormal condition is:

$$\langle q_n | q_{n'} \rangle = \delta_{n,n'} \equiv \begin{cases} 0, & n \neq n' \\ 1, & n = n' \end{cases}$$

How do we handle situations where the eigenvalue spectrum is ***continuous***?

$$\langle x | x' \rangle = \delta(x - x') \equiv \begin{cases} 0, & x \neq x' \\ \infty, & x = x' \end{cases}$$

Notice that $\int_{-\infty}^{\infty} dx\, \delta(x - x') = 1$.

What' the unit of $\delta(x)$?

**Example**

The wave function of a particle exactly localized at a particular location $x'$ is $\delta(x - x')$.

$$| x' \rangle = \int_{-\infty}^{\infty} dx\, \delta(x - x') | x \rangle$$

Mathematical interpretation: Since $\int_{-\infty}^{\infty} dx\, \delta(x - x') f(x) = f(x')$, we have $\int_{-\infty}^{\infty} dx\, \delta(x - x') | x \rangle = | x' \rangle$.

Consider another state $|x''\rangle$, in which the particle is localized at $x''$.

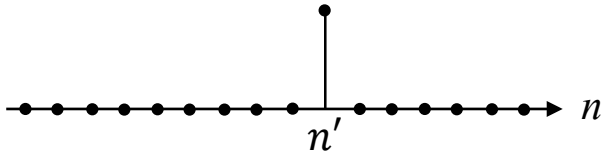
$$\langle x'' | x' \rangle = \langle x'' | \int_{-\infty}^{\infty} dx\, \delta(x - x') | x \rangle = \int_{-\infty}^{\infty} dx\, \delta(x - x') \langle x'' | x \rangle$$

$$= \int_{-\infty}^{\infty} dx\, \delta(x - x') \delta(x - x'') = \delta(x' - x'') = \delta(x'' - x')$$

$$x'' \to x \quad \Rightarrow \quad \langle x | x' \rangle = \delta(x - x')$$

This exercise is to show consistency of the definition of normalization for the continuous case, ***not*** attempting at any mathematical "proof".

Discrete

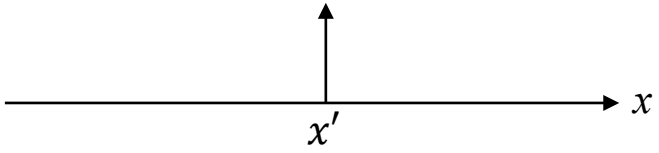



$$\langle q_n | q_{n'} \rangle = \delta_{n,n'} \equiv \begin{cases} 0, & n \neq n' \\ 1, & n = n' \end{cases}$$

System in a particular eigenstate

$$\sum_n \langle q_n | q_{n'} \rangle = \sum_n \delta_{n,n'} = 1$$

Continuous




$$\langle x | x' \rangle = \delta(x - x') \equiv \begin{cases} 0, & x \neq x' \\ \infty, & x = x' \end{cases}$$

Particle at a particular location

$$\int_{-\infty}^{\infty} dx \, \langle x | x' \rangle = \int_{-\infty}^{\infty} dx \, \delta(x - x') = 1$$

Now you see, the two definitions of normalization are indeed equivalent.

Recall that $\delta(x - x')$ is the limiting case of a "pulse" (actually "packet" in space) at $x'$.

The definition is general, not just for position $x$. Applied to momentum: $\langle p | p' \rangle = \delta(p - p')$.

Now we can re-examine the normalization of our momentum eigenstate $|p\rangle$:

$$|p\rangle = \int_{-\infty}^{\infty} dx \, \psi_p(x) \, |x\rangle$$

For more details about dimensions/units, see the **FYI slides** below (not discussed in class).

Re-examine the normalization of our momentum eigenstate $|p\rangle = \int_{-\infty}^{\infty} dx\, \psi_p(x)\, |x\rangle$

Let $\langle x|p\rangle = \psi_p(x) = c_p e^{ikx}$, where $c_p$ is the normalization constant.

Taking conjugates for the bra

$$\langle p|p'\rangle = \boxed{\int_{-\infty}^{\infty} dx\, \psi_p^*(x)\langle x|} \int_{-\infty}^{\infty} dx'\, \psi_{p'}(x')|x'\rangle$$

$$= \int_{-\infty}^{\infty} dx c_p^* e^{-ikx}\langle x| \int_{-\infty}^{\infty} dx' c_{p'} e^{ik'x'}|x'\rangle$$

$$= \int_{-\infty}^{\infty} dx c_p^* e^{-ikx} \int_{-\infty}^{\infty} dx' c_{p'} e^{ik'x'}\langle x|x'\rangle$$

$$= \int_{-\infty}^{\infty} dx c_p^* e^{-ikx} \int_{-\infty}^{\infty} dx' c_{p'} e^{ik'x'}\, \delta(x'-x)$$

$$= \int_{-\infty}^{\infty} dx c_p^* e^{-ikx}\, c_{p'} e^{ik'x}$$

$$= \int_{-\infty}^{\infty} dx c_p^* c_{p'} e^{i(k'-k)x}$$

$$= 2\pi c_p^* c_{p'}\, \delta(k-k')$$

$$= 2\pi\hbar c_p^* c_{p'}\, \delta(p-p')$$

$$= 2\pi\hbar |c_p|^2\, \delta(p-p')$$

$$= \delta(p-p')$$

**Notes**

Using $|p\rangle = \int_{-\infty}^{\infty} dx\, \psi_p(x)\, |x\rangle$

Inserting $\psi_p(x) = c_p e^{ikx}$

Using $\langle x|x'\rangle = \delta(x'-x)$

Using $\int_{-\infty}^{\infty} dx'\, \delta(x'-x) f(x') = f(x); f(x') = e^{ik'x'}$

Using $\int_{-\infty}^{\infty} dx e^{i(k'-k)x} = 2\pi\, \delta(k-k')$

Using $\delta(ax) = \delta(x)/|a|$ and $p = \hbar k$

see **FYI slides**

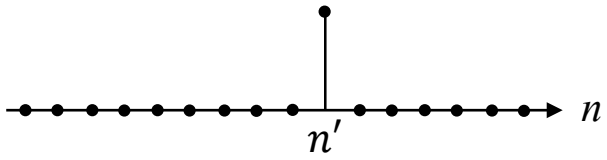
$c_{p'} = c_p$ when $p = p'$

Therefore, $2\pi\hbar|c_p|^2 = 1 \Rightarrow c_p = \frac{1}{\sqrt{2\pi\hbar}} \Rightarrow \boxed{\langle x|p\rangle = \psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ikx}}$

For more details about dimensions/units, see the **FYI slides** below (not discussed in class).

# FYI: More on normalization of eigenstates of continuous spectra (not discussed in class)

Discrete: Quantity $Q$ has eigenvalues $q_n$ corresponding to eigenstates $|n\rangle$

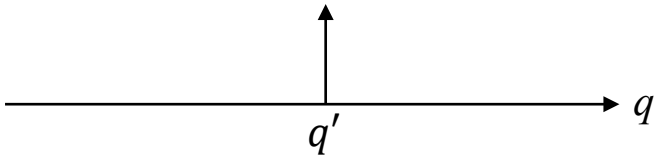



$$\langle q_n|q_{n'}\rangle = \delta_{n,n'} \equiv \begin{cases} 0, & n \neq n' \\ 1, & n = n' \end{cases}$$

$$\sum_n \langle q_n|q_{n'}\rangle = \sum_n \delta_{n,n'} = 1$$

$\langle q_n|q_{n'}\rangle = \delta_{n,n'}$ are dimensionless.

Continuous: Quantity $Q$ has eigenvalues $q$ corresponding to eigenstates $|q\rangle$




$$\langle q|q'\rangle = \delta(q-q') \equiv \begin{cases} 0, & q \neq q' \\ \infty, & q = q' \end{cases}$$

$$\int_{-\infty}^{\infty} dq\, \langle q|q'\rangle = \int_{-\infty}^{\infty} dq\, \delta(q-q') = 1$$

$\langle q|q'\rangle = \delta(q-q')$ are of dimension $\mathrm{Q}^{-1}$.

So, it is reasonable to assign $|q\rangle$ the dimension $\mathrm{Q}^{-1/2}$, since the bra and ket are of the same dimension.

Now we see, $|x\rangle$ is of dimension $\mathrm{l}^{-1/2}$ (l is length),
and $|p\rangle$ is of dimension $\mathrm{p}^{-1/2}$ (p is momentum), if the spectrum for $p$ is continuous.

Therefore, $\langle x|p\rangle$ is of dimension $(\mathrm{lp})^{-1/2}$.

$$\langle x|p\rangle = \psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}\, e^{ikx}$$

Recall that $\hbar$ has the dimension of angular momentum, which is $(\mathrm{lp})^{-1/2}$.
Thus we see, $\langle x|p\rangle$ is indeed of dimension $(\mathrm{lp})^{-1/2}$.

## FYI (not discussed in class)

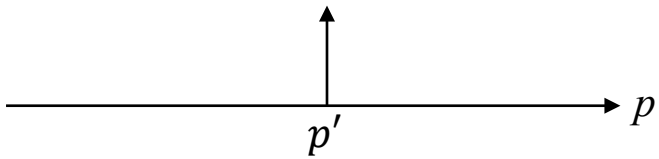
In general, for any $Q$ with a continuous spectrum, $|q\rangle$ is of dimension $\mathrm{Q}^{-1/2}$ and $\langle x|q\rangle$ is of dimension $(\mathrm{lQ})^{-1/2}$.

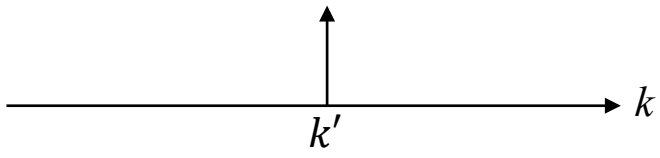
On the other hand, for any $Q$ with a discrete spectrum, $|n\rangle$ is of dimensionless and $\langle x|n\rangle$ is of dimension $\mathrm{l}^{-1/2}$.

---

With $p = \hbar k$, let's now examine $|p\rangle$ and $|k\rangle$.

$|p\rangle$ dimension $\mathrm{p}^{-1/2}$ (p is momentum),
$|k\rangle$ dimension $(\mathrm{l}^{-1})^{-1/2}$.




$$\langle p|p'\rangle = \delta(p-p') \equiv \begin{cases} 0, & p \neq p' \\ \infty, & p = p' \end{cases}$$

$$\langle k|k'\rangle = \delta(k-k') \equiv \begin{cases} 0, & k \neq k' \\ \infty, & k = k' \end{cases}$$

$$\int_{-\infty}^{\infty} dp\, \langle p|p'\rangle = \int_{-\infty}^{\infty} dp\, \delta(p-p') = 1$$

$$\int_{-\infty}^{\infty} dk\, \langle k|k'\rangle = \int_{-\infty}^{\infty} dk\, \delta(k-k') = 1$$

$\langle p|p'\rangle = \delta(p-p')$ are of dimension $\mathrm{p}^{-1}$.

$\langle k|k'\rangle = \delta(k-k')$ are of dimension $(\mathrm{l}^{-1})^{-1}$.

$$\int_{-\infty}^{\infty} dp\, \langle p|p'\rangle = \int_{-\infty}^{\infty} dp\, \delta(p-p') = \int_{-\infty}^{\infty} d(\hbar k)\, \delta(\hbar k - \hbar k') = \int_{-\infty}^{\infty} dk\, \delta(k-k') = \int_{-\infty}^{\infty} dk\, \langle k|k'\rangle = 1$$

Using $\delta(ax) = \delta(x)/|a|$ and $p = \hbar k$

## FYI (not discussed in class)

$$\int_{-\infty}^{\infty} dp\,\langle p|p'\rangle = \int_{-\infty}^{\infty} dp\,\delta(p-p') = \int_{-\infty}^{\infty} d(\hbar k)\,\delta(\hbar k-\hbar k') = \int_{-\infty}^{\infty} dk\,\delta(k-k') = \int_{-\infty}^{\infty} dk\,\langle k|k'\rangle = 1$$

Using $\delta(ax) = \delta(x)/|a|$ and $p = \hbar k$

$$\Rightarrow \qquad dp\,\langle p|p'\rangle = dk\,\langle k|k'\rangle$$

$$\Rightarrow \qquad \langle k|k'\rangle = \frac{dp}{dk}\langle p|p'\rangle = \hbar\langle p|p'\rangle \qquad \Rightarrow \qquad |k\rangle = \sqrt{\hbar}|p\rangle$$

$$\langle x|p\rangle = \psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}\,e^{ikx} \qquad \Rightarrow \qquad \psi_k(x) \equiv \langle x|k\rangle = \sqrt{\hbar}\,\langle x|p\rangle = \frac{1}{\sqrt{2\pi}}\,e^{ikx}$$

Wave function of state $|p\rangle$

Wave function of state $|k\rangle$

An arbitrary state $|\psi\rangle = \int_{-\infty}^{\infty} dx\,\psi(x)\,|x\rangle$ can be expanded as a linear combination of states $|p\rangle$ or a linear combination of states $|k\rangle$.

Try to appreciate as much of the following as you can.
We will be kind of "derive" the **Fourier transform**.

$$\psi(x) = \langle x|\psi\rangle$$

insert

$$|\psi\rangle = \int_{-\infty}^{\infty} dx\,\psi(x)\,|x\rangle \qquad \Rightarrow \qquad |\psi\rangle = \int_{-\infty}^{\infty} dx\langle x|\psi\rangle\,|x\rangle = \int_{-\infty}^{\infty} dx|x\rangle\langle x|\psi\rangle$$

$\int_{-\infty}^{\infty} dx|x\rangle\langle x|=1$ can be viewed as an identity operator. All $|x\rangle$ make a complete basis set.

## FYI (not discussed in class)

To expand an arbitrary state $|\psi\rangle = \int_{-\infty}^{\infty} dx \langle x|\psi\rangle\, |x\rangle = \int_{-\infty}^{\infty} dx |x\rangle\langle x|\psi\rangle$ as a linear combination of states $|p\rangle$, we need to find the "weights" $\langle p|\psi\rangle \equiv \phi_p(p)$.

$$\phi_p(p) \equiv \langle p|\psi\rangle = \langle p| \int_{-\infty}^{\infty} dx |x\rangle\langle x|\psi\rangle = \int_{-\infty}^{\infty} dx \langle p|x\rangle \langle x|\psi\rangle = \int_{-\infty}^{\infty} dx \, (\langle x|p\rangle)^* \langle x|\psi\rangle$$

insert $\langle x|p\rangle = \psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ikx}$

insert $\psi(x) = \langle x|\psi\rangle$

We put a subscript $p$ here just to make $\phi_p(p)$ look different from $\phi(k)$, the weights of $|\psi\rangle$ when expanded onto $|k\rangle$.

$$\Rightarrow \quad \phi_p(p) \equiv \langle p|\psi\rangle = \int_{-\infty}^{\infty} dx \, [\psi_p(x)]^* \psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx e^{-ikx} \psi(x)$$

You see, this is simply the Fourier transform from "space domain" to "momentum domain":

$$\phi_p(p) \equiv \langle p|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx e^{-ikx} \psi(x)$$

Alternatively, we can expand $|\psi\rangle$ as a linear combination of states $|k\rangle$, with "weights" $\langle k|\psi\rangle \equiv \phi(p)$.

$$\phi(k) \equiv \langle k|\psi\rangle = \langle k| \int_{-\infty}^{\infty} dx |x\rangle\langle x|\psi\rangle = \int_{-\infty}^{\infty} dx \langle k|x\rangle \langle x|\psi\rangle = \int_{-\infty}^{\infty} dx \, (\langle x|k\rangle)^* \langle x|\psi\rangle$$

FYI (not discussed in class)

$$\phi(k) \equiv \langle k|\psi\rangle = \langle k| \int_{-\infty}^{\infty} dx|x\rangle\langle x|\psi\rangle = \int_{-\infty}^{\infty} dx\langle k|x\rangle \langle x|\psi\rangle = \int_{-\infty}^{\infty} dx \, (\langle x|k\rangle)^* \langle x|\psi\rangle$$

insert

insert

$$\psi_k(x) \equiv \langle x|k\rangle = \sqrt{\hbar}\,\langle x|p\rangle = \frac{1}{\sqrt{2\pi}} e^{ikx}$$

$$\psi(x) = \langle x|\psi\rangle$$

$$\Rightarrow \quad \phi(k) \equiv \langle k|\psi\rangle = \int_{-\infty}^{\infty} dx \, [\psi_k(x)]^* \psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx e^{-ikx} \psi(x)$$

This is simply the Fourier transform from "space domain" to "wavevector domain":

$$\phi(k) \equiv \langle k|\psi\rangle = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx e^{-ikx} \psi(x)$$

Compare this with the Fourier transform to "momentum domain":

$$\phi_p(p) \equiv \langle p|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx e^{-ikx} \psi(x)$$

You see, there is a difference in the pre-factor.

We just discovered Fourier transformation!

These are the conclusions relevant to our following discussion on wave packets.

**Added notes**: Calculate the inner product of two states by their wave forms

On slide 32, we showed that $\langle p|p'\rangle = \delta(p-p')$, by actually showing that

$$\langle p|p'\rangle = \int_{-\infty}^{\infty} dx \langle x|x\rangle \langle x|\psi\rangle = \int_{-\infty}^{\infty} dx c_p^* e^{-ikx}\ c_{p'} e^{ik'x} = \int_{-\infty}^{\infty} dx\, \psi_p^*(x)\, \psi_{p'}(x'),$$

where $\psi_p = \langle x|p\rangle$ thus $|p\rangle = \int_{-\infty}^{\infty} dx\, \psi_p(x)\, |x\rangle$.

This is just a special case of the inner product of two states: $\langle \psi_1|\psi_2\rangle = \int_{-\infty}^{\infty} dx\, \psi_1^*(x)\, \psi_2(x')$

Here, we give the proof for the general case.

For an arbitrary state $|\psi\rangle$, we have it wave function $\psi(x) = \langle x|\psi\rangle$ thus $|\psi\rangle = \int_{-\infty}^{\infty} dx\, \psi(x)\, |x\rangle$.

Therefore, the bra $\langle \psi_1| = \int_{-\infty}^{\infty} dx\, \langle x|\psi_1^*(x)$.

Since we are handling two independent integrals, we write the ket as $|\psi_2\rangle = \int_{-\infty}^{\infty} dx\, \psi_2(x)\, |x\rangle$.

Thus,

$$\langle \psi_1|\psi_2\rangle = \int_{-\infty}^{\infty} dx\, \langle x|\ \psi_1^*(x) \int_{-\infty}^{\infty} dx'\, \psi_2(x')\ |x'\rangle$$ By inserting the above.

$$= \int_{-\infty}^{\infty} dx\, \psi_1^*(x)\, \langle x| \int_{-\infty}^{\infty} dx'\, \psi_2(x')\ |x'\rangle = \int_{-\infty}^{\infty} dx\, \psi_1^*(x) \int_{-\infty}^{\infty} dx'\, \psi_2(x') \langle x|x'\rangle$$

$$= \int_{-\infty}^{\infty} dx\, \psi_1^*(x) \int_{-\infty}^{\infty} dx'\, \psi_2(x') \delta(x-x')$$ Using $\langle x|x'\rangle = \delta(x'-x)$

(to be cont'd)

$$\langle \psi_1 | \psi_2 \rangle = \int_{-\infty}^{\infty} dx \, \langle x | \, \psi_1^*(x) \int_{-\infty}^{\infty} dx' \, \psi_2(x') \, |x'\rangle$$

$$= \int_{-\infty}^{\infty} dx \, \psi_1^*(x) \int_{-\infty}^{\infty} dx' \, \psi_2(x') \delta(x - x')$$

$$= \int_{-\infty}^{\infty} dx \, \psi_1^*(x) \, \psi_2(x)$$

By using Using $\int_{-\infty}^{\infty} dx' \, \delta(x' - x) f(x') = f(x)$

QED.

We sometimes need to find the "matrix element" of an operator $Q_{12} = \langle \psi_1 | \mathrm{Q} | \psi_2 \rangle$. This is just the inner product of state $|\psi_1\rangle$, represented by bra $\langle \psi_1|$ here and a new state $\mathrm{Q}|\psi_2\rangle$. Therefore,

$$Q_{12} = \langle \psi_1 | \mathrm{Q} | \psi_2 \rangle = \int_{-\infty}^{\infty} dx \, \psi_1^*(x) \, \mathrm{Q} \psi_2(x).$$

In the special case $|\psi_1\rangle = |\psi_2\rangle = |\psi\rangle$, we find the average for quantity $Q$ in state $|\psi\rangle$:

$$\langle Q \rangle = \int_{-\infty}^{\infty} dx \, \psi^*(x) \, \mathrm{Q} \psi(x).$$

# Re-examine the wave function form of Schrödinger equation

We introduced the Schrödinger equation in the wave function form in a hand-waving manner. Finally, we can now justify the following:

Let $|p\rangle$ be an momentum eigenstate with eigenvalue $p$, we can then write:

momentum operator

momentum eigenvalue

$$\mathrm{p}|p\rangle = p|p\rangle \Rightarrow \langle x|\mathrm{p}|p\rangle = p\,\langle x|p\rangle \Rightarrow \mathrm{p}\,\langle x|p\rangle = p\,\langle x|p\rangle$$

momentum eigenstate corresponding to eigenvalue $p$

This step will be discussed later.

Now.

Inserting the wave function of the momentum eigenstate $\langle x|p\rangle \equiv \psi_p(x)$, we get:

$$\mathrm{p}\,\psi_p(x) = p\,\psi_p(x) \qquad (1)$$

"Knowing" $\psi_p(x) = e^{ikx}$ with $k = p/\hbar$, we concluded $\boxed{\mathrm{p} = -i\hbar\frac{d}{dx}}$

$|p\rangle = \int_{-\infty}^{\infty} dx\, \psi_p(x)\, |x\rangle$ $\quad$ $\langle x|p\rangle = \psi_p(x)$

insert

$\mathrm{p}|p\rangle = p|p\rangle \Rightarrow \langle x|\mathrm{p}|p\rangle = p\,\langle x|p\rangle$

$$\langle x|\,\mathrm{p}\int_{-\infty}^{\infty} dx'\,\psi_p(x')\,|x'\rangle = p\,\psi_p(x)$$

Consider $x'$ as the variable to be integrated over and $x$ as a particular value

$$\Rightarrow \quad \mathrm{p}\int_{-\infty}^{\infty} dx'\,\psi_p(x')\,\langle x|x'\rangle = p\,\psi_p(x)$$

$$\Rightarrow \mathrm{p}\int_{-\infty}^{\infty} dx'\,\psi_p(x')\,\delta(x'-x) = p\,\psi_p(x)$$

Using $\langle x|x'\rangle = \delta(x'-x)$

$$\Rightarrow \qquad \mathrm{p}\,\psi_p(x) = p\,\psi_p(x)$$

Using $\int_{-\infty}^{\infty} dx' f(x')\,\delta(x'-x) = f(x)$

This is the momentum eigenvalue equation in the wave function form. (Only a ***free particle*** is in a momentum eigenstate.)

No state vectors in this equation now; we consider $\mathrm{p}\,\psi_p(x)$ as the operator operating on the function $\psi_p(x)$, which can be viewed as an infinite-dimensional 1-column matrix, i.e. vector.

We already know $\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ikx}$.

We also know that the derivative of an exponential function $\propto$ itself.

Taking care of prefactors as we did, we got:

$$\mathrm{p} = -i\hbar \frac{d}{dx}$$

# Particle as wave packet

We paused here on Tue 2/14/2023.

For simplicity, we considered a free particle in 1D. Its **normalized** wave function is a plane wave propagating at a velocity $v = p/m = \hbar k/m$:

$$\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ikx}$$

We now extend this into 3D. The **normalized** wave function is:

$$\psi_{\mathbf{p}}(\boldsymbol{r}) = \left(\frac{1}{\sqrt{2\pi\hbar}}\right)^3 e^{i\boldsymbol{k}\cdot\boldsymbol{r}}, \text{ where } \boldsymbol{r} = x\hat{\boldsymbol{x}} + y\hat{\boldsymbol{y}} + z\hat{\boldsymbol{z}} \text{ and } \boldsymbol{k} = k_x\hat{\boldsymbol{x}} + k_y\hat{\boldsymbol{y}} + k_z\hat{\boldsymbol{z}}$$

Just a plane wave propagating in the direction of $\boldsymbol{k}$ at a velocity $\boldsymbol{v} = \boldsymbol{p}/m = \hbar\boldsymbol{k}/m$.

Does this make sense?

A free particle in free space moving at a velocity $\boldsymbol{v} = \boldsymbol{p}/m = \hbar\boldsymbol{k}/m$, yet it is all over the place with an equal probability $|\psi_p(\mathbf{r})|^2 = \left(\frac{1}{2\pi\hbar}\right)^3$ for all $\boldsymbol{r}$. The overall probability is $\int_{-\infty}^{\infty} dx |\psi_{\mathbf{p}}(x)|^2 = \infty$.

Yes, it makes sense.

We encountered similar situations in classical physics. Consider an electromagnetic (EM) plane wave propagating at a velocity $\boldsymbol{v} = (\frac{\omega}{k})\hat{\boldsymbol{k}}$. The intensity $|\boldsymbol{E}(\boldsymbol{r})|^2$ = constant for all $\boldsymbol{r}$. The overall power $\propto \int d^3\boldsymbol{r}\, |\boldsymbol{E}(\boldsymbol{r})|^2 = \infty$. We should have complained!

An EM pulse is a wave packet; an electron is a wave packet (see animation next page).

To keep it simple, we go back to 1D.

By Fourier transformation, an arbitrary state $|\psi\rangle = \int_{-\infty}^{\infty} dx\, \psi(x)\, |x\rangle$ is expanded as a linear combination of plane wave states $|k\rangle$, with the "weights" $\langle k|\psi\rangle \equiv \phi(k)$:

$$\langle k|\psi\rangle = \int_{-\infty}^{\infty} dx\, \psi(x) \langle k|x\rangle \quad \leftarrow \text{insert} \quad \langle k|x\rangle = \langle x|k\rangle^* = e^{-ikx}$$

$$\Downarrow$$

$$\boxed{\phi(k) \equiv \langle k|\psi\rangle = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx e^{-ikx}\, \psi(x)}$$

The inverse transformation: $\boxed{\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk e^{ikx}\, \phi(k)}$ The spectrum, i.e. amplitudes of plane waves $|k\rangle$.

This is similar to the Fourier transform between a time domain signal and its frequency spectrum. Wave vector $k$ is the spatial equivalent of angular frequency.

For a time-domain pulse, the product of pulse width and its spectral width $\Delta t \Delta\omega \sim 1$.

Similarly for a wave packet, the product of packet width and its spectral width, $\Delta x \Delta k \sim 1$.

Since $p = \hbar k$, we have $\boxed{\Delta x\, \Delta p \sim \hbar}$.

The "uncertainty principle" of position and momentum

Let's first visually appreciate the propagation of a wave packet through space and time.

(Dispersionless first, for simplicity)

Now consider wave packet propagation mathematically.

$$\psi(x,0)=\psi(x)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}dke^{ikx}\,\phi(k)$$

https://en.wikipedia.org/wiki/Wave_packet

$$\psi(x,t)=e^{-i\omega t}\psi(x)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}dke^{i(kx-\omega t)}\,\phi(k)$$

If $\omega \propto |k|$, e.g., $\omega = c|k|$ for EM waves in free space,

$$E(x,t)=e^{-i\omega t}E(x)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}dke^{ik(x-ct)}\,\phi(k)$$

The wave packet $E(x)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}dke^{ikx}\,\phi(k)$ simply moves at the phase velocity $c$ without changing its shape. This is the dispersionless case.

For visualization, **closely** watch the above animation (*A wave packet **without** dispersion*) at https://en.wikipedia.org/wiki/Wave_packet.

## Wave packet dispersion

For EM waves in a general medium or the electron (or any particle) wave $\psi(x,t)$, $\omega = \omega(k)$ is ***nonlinear***. The wave packet will propagate, but its shape will change and the packet will distort and broaden.
This phenomenon is called dispersion.

For visualization, **closely** watch a second animation (*A wave packet **with** dispersion*) at https://en.wikipedia.org/wiki/Wave_packet and compare with the first one (*A wave packet **without** dispersion*; copied here for easy comparison).

*A wave packet **without** dispersion*

*A wave packet **with** dispersion*

For the electron (or any particle) wave $\psi(x,t)$, called the de Broglie wave, $\omega = \omega(k)$ is very nonlinear! $\omega \propto k^2 \Rightarrow$ very dispersive!

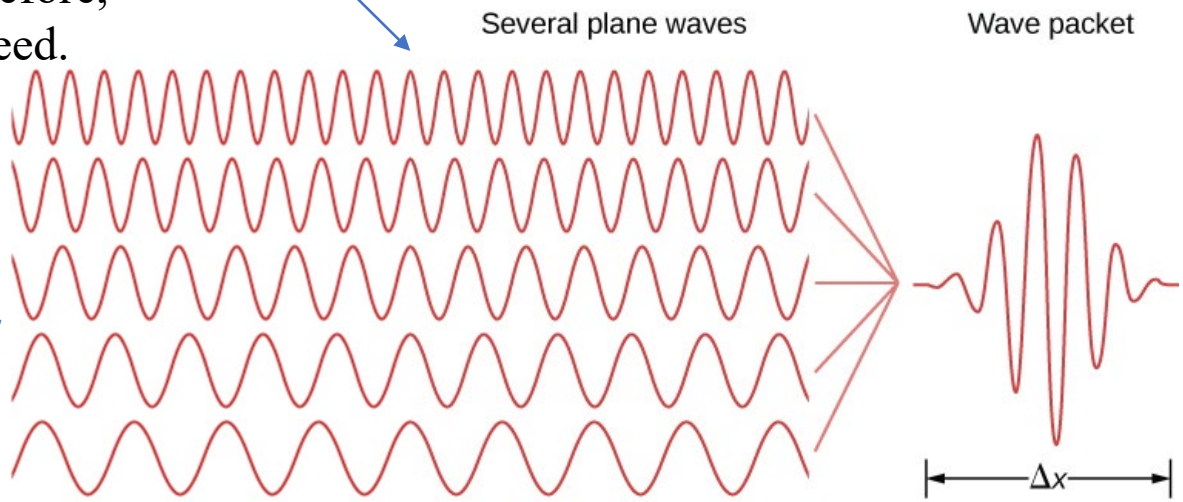
A true understanding of wave packets, interference, group velocity, uncertain principle, etc.

The center of the wave packet is where all plane waves of different $k$ (or wavelength) are in phase.

(constructively interfere)

If $\omega \propto |k|$, all plane waves propagate at the same phase velocity. Therefore, the center moves at the same speed.

No dispersion.




$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk e^{i[kx-\omega(k)t]} \phi(k)$$

At the wave packet center $x_c$, constructive interference requires $\frac{\partial}{\partial k}[kx_c - \omega(k)t] = 0$.

$$\Rightarrow \quad x_c - \frac{d\omega}{dk} t = 0$$

$$\Rightarrow \quad x_c = \frac{d\omega}{dk} t$$

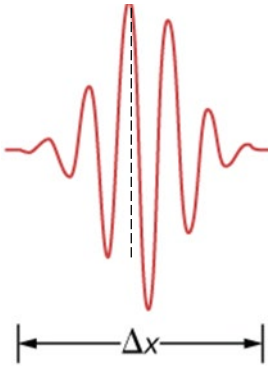



Illustration adapted from an image at

https://phys.libretexts.org/TextBooks_and_TextMaps/University_Physics/Book%3A_University_Physics_(OpenStax)/Map%3A_University_Physics_III_-_Optics_and_Modern_Physics_(OpenStax)/7%3A_Quantum_Mechanics/7.2%3A_The_Heisenberg_Uncertainty_Principle

Thus, the center of the wave packet moves at a speed $\boxed{\frac{d\omega}{dk} \equiv v_g}$, called the group velocity.

With dispersion, while the center of the wave packet moves at the group velocity $\frac{d\omega}{dk} \equiv v_g$, the relative phase of a component plane wave $k$ with regard to the plane wave of central wave vector $k_c$ varies with time.

Therefore, the wave packet changes shape and usually broadens.

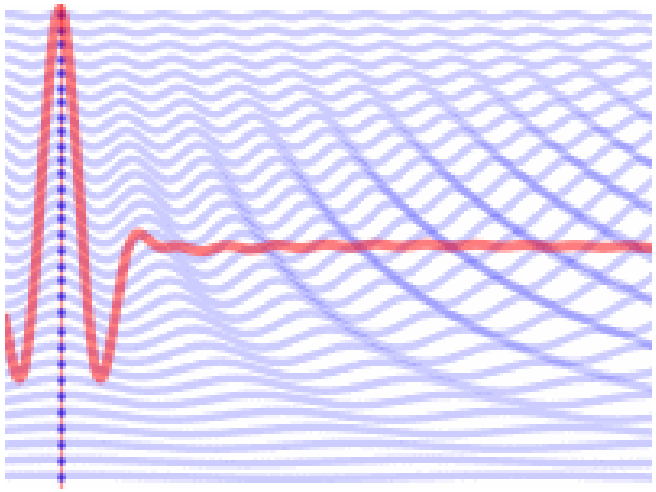
For visualization, again **closely** watch the second animation (A wave packet **with** dispersion) at https://en.wikipedia.org/wiki/Wave_packet.

For the electron (or any particle) wave $\psi(x,t)$, called the de Broglie wave, $\omega = \omega(k)$ is very nonlinear! $\omega \propto k^2 \Rightarrow$ very dispersive!

For visualization, **closely** watch animation at https://en.wikipedia.org/wiki/Wave_packet under *Gaussian wave packets in **quantum mechanics***:

https://en.wikipedia.org/wiki/Wave_packet#/media/File:Wavepacket1.gif

This is the real (or imaginary) part **only**.

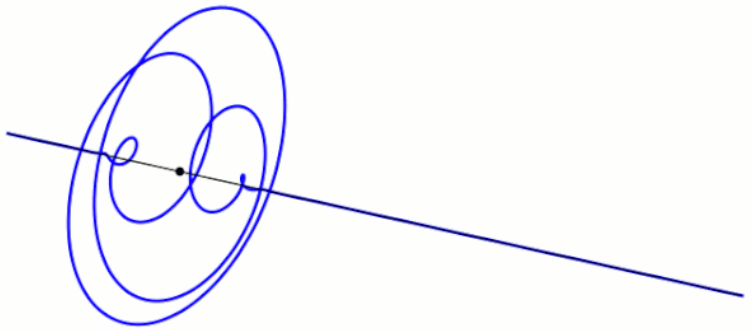


Blue: component plane waves

Red: wave packet

The wave function is complex. So for a full picture, watch the third animation under the same heading:

https://en.wikipedia.org/wiki/Wave_packet#/media/File:Wavepacket-a2k4-en.gif



Recall that $|\psi(x)|^2$ is the probability density. To see how the envelope of probability density propagates and evolves, watch the animation under the heading *Basic behaviors*: subheading *Dispersive*:

https://en.wikipedia.org/wiki/Wave_packet#/media/File:Guassian_Dispersion.gif

# Highlights and Remarks

Quantum mechanics is not weird.

We are familiar with waves, superposition, and coherence.

A possible reason it may look hard/weird:

For other waves, both the amplitude and the intensity are observable quantities.

In quantum mechanics, the amplitude *per se* is not observable while the analog of intensity is probability.

Analogy helps. Stationary states are like modes of electromagnetic wave.

But, we also notice differences.

Physical quantities are real. ⇒ Amplitudes of other waves are real. We use complex numbers as a math tool. For example, a single tone is the sum of a positive- and a negative-frequency Fourier component.

Amplitudes in quantum mechanics are complex.

Schrödinger equation vs. other wave equations.

$$\nabla^2 \psi(\mathbf{r}) = -\frac{2m}{\hbar^2}[\hbar\omega - V(\mathbf{r})]\psi(\mathbf{r}) \quad \text{vs.} \quad \nabla^2 \psi(\mathbf{r}) = -\frac{\omega^2}{c^2} n^2 \psi(\mathbf{r}) \quad \text{for stationary states.}$$

A quantity e.g. $E_z$, $V$ or $I$ in 1D transmission line

Refractive index

There are no 1D dielectric cavities!

$i$ vs. $j$ as $\sqrt{-1}$.

$e^{-i\omega t}$ vs. $e^{j\omega t}$

$e^{i(kx-\omega t)}$ vs. $e^{j(\omega t-kx)}$

We are familiar with the vector space, linear algebra.

Again, complex amplitudes *per se* are not observable in quantum mechanics.

Amplitudes in quantum mechanics are complex.

Inner products involve taking complex conjugates.

(The bra is the conjugate transpose of the ket)

Complex amplitudes are used elsewhere for mathematical convenience.

Limited scope of Part I and Part II this QM primer: one-particle