

What makes Quantum Physics different from earlier Physics?

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Quantum physics vs classical physics

- 1. The experiments**
- 2. The theory**
- 3. Bonus track**

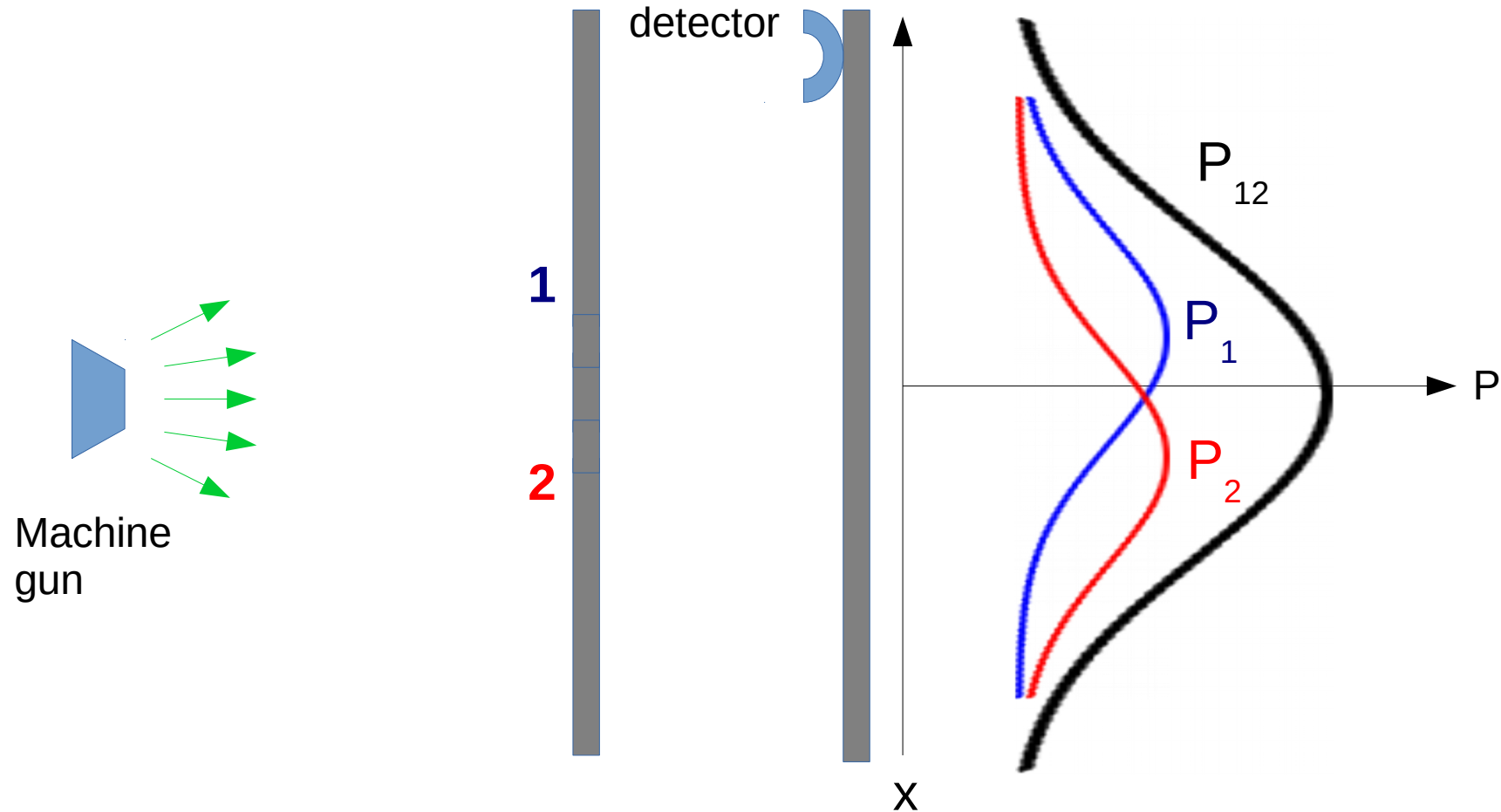
Quantum physics vs classical physics

1. The experiments

2. The theory

3. Bonus track

An experiment with bullets

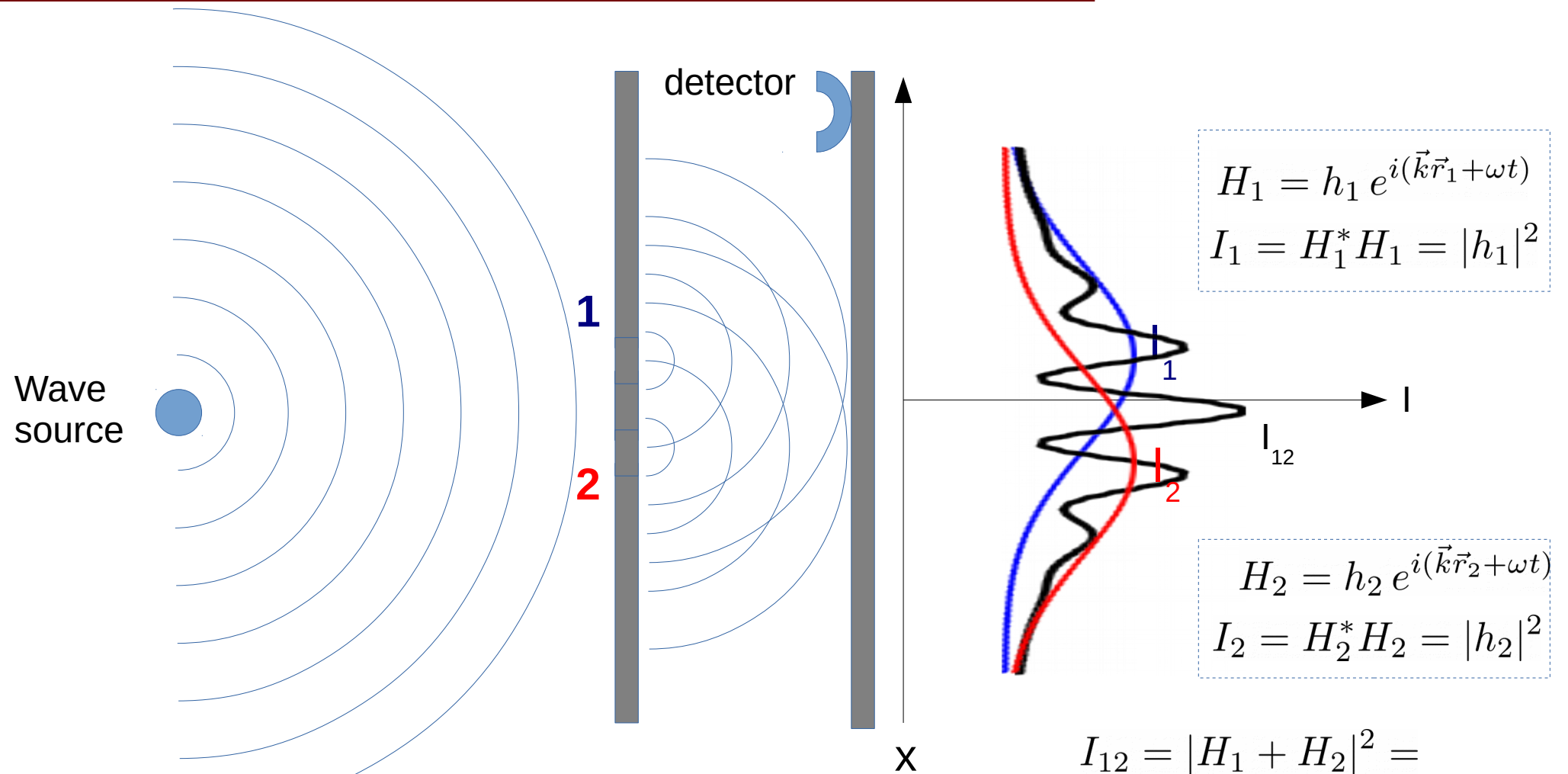


a) Detection in lumps (discrete clicks, identical loudness)

b) $P_{12} = P_1 + P_2$

Particle signatures

An experiment with waves

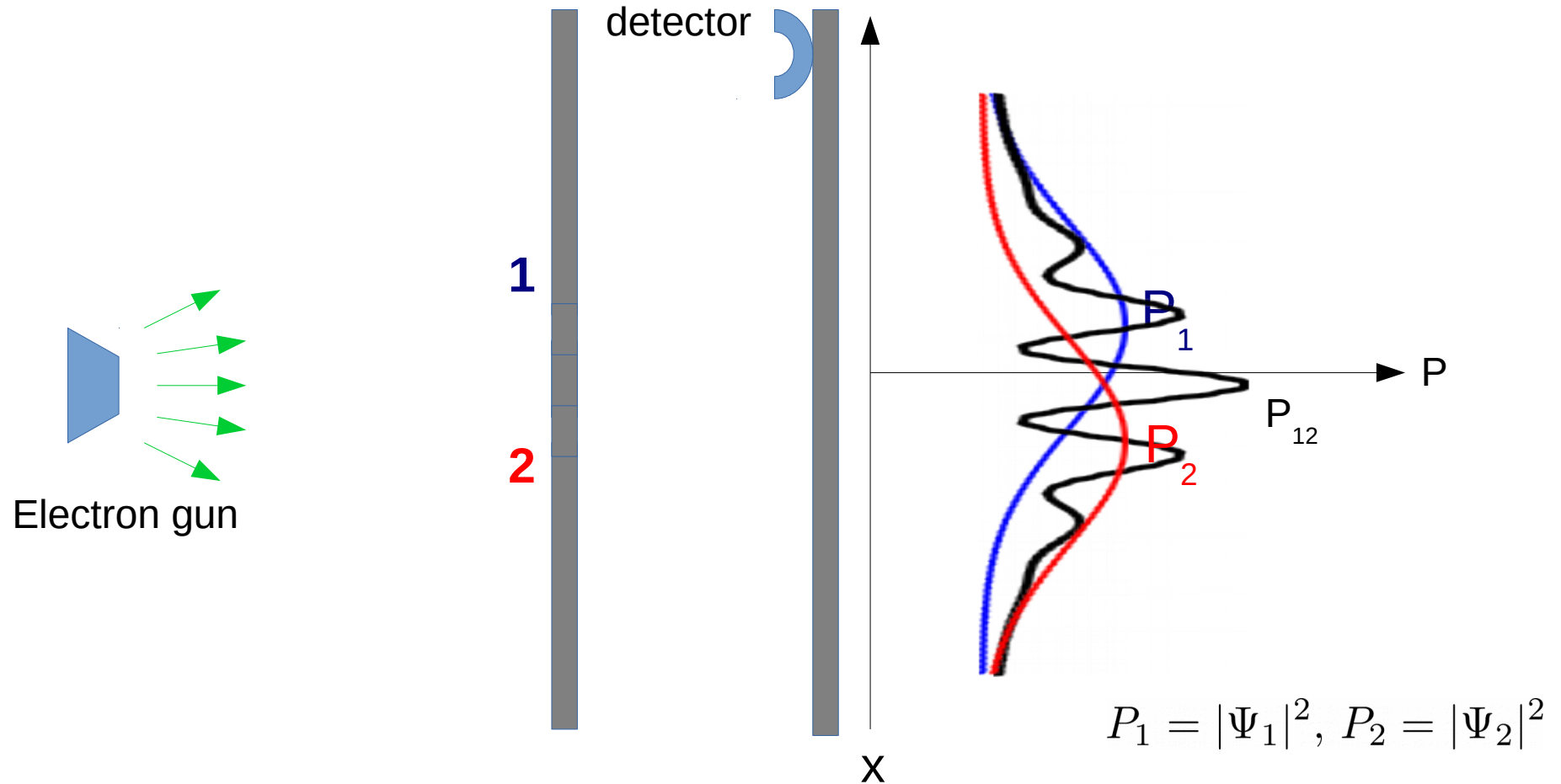


a) Detection continuous (variable loudness)

b) $I_{12} = |H_1 + H_2|^2 \neq I_1 + I_2$

Wave signatures 5

An experiment with electrons

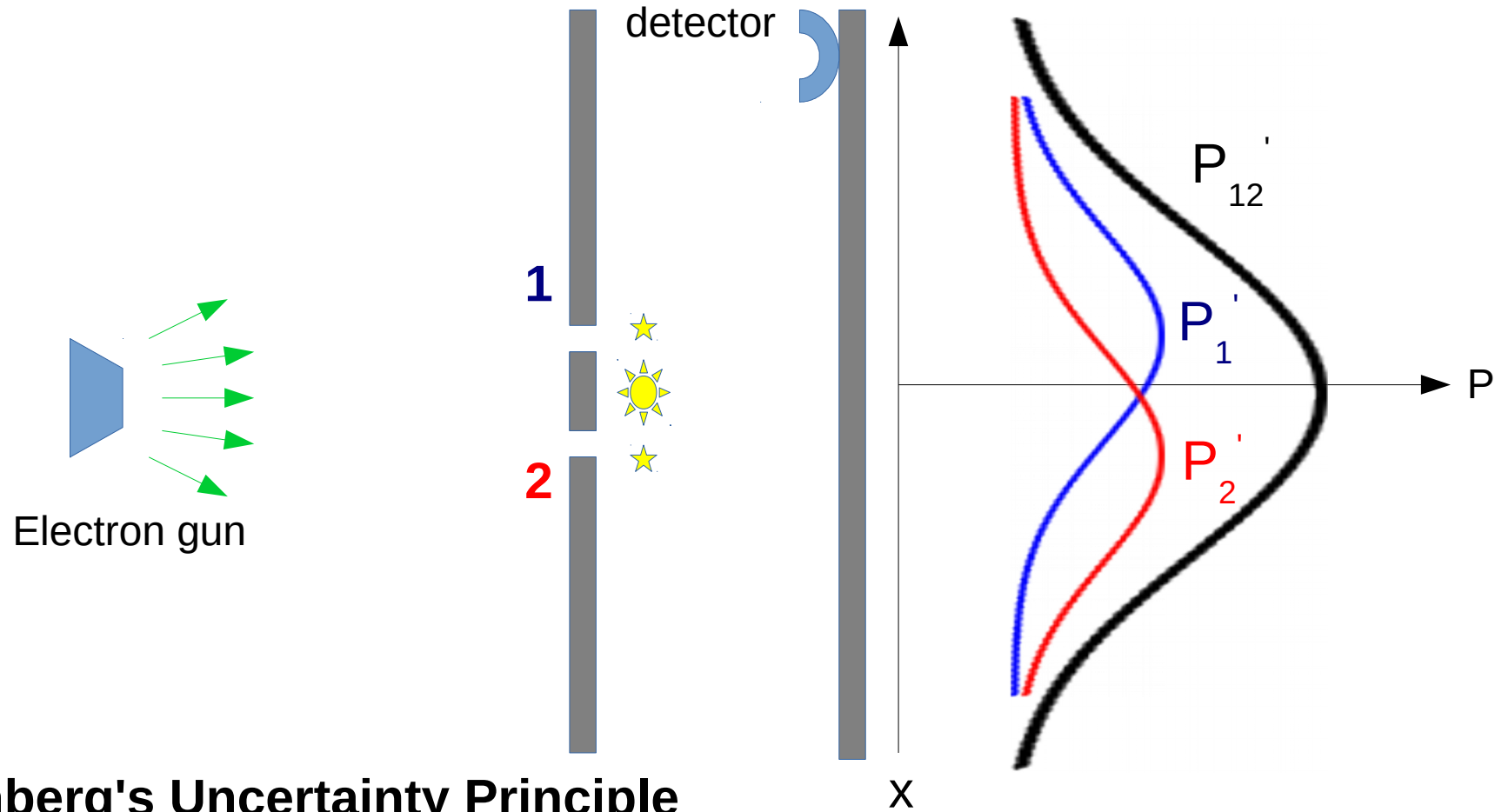


a) Detection in lumps (discrete clicks, identical loudness)

b) $I_{12} = |\psi_1 + \psi_2|^2 \neq P_1 + P_2$

***Dual nature:
particle-wave***

Let's watch the electrons



Heisenberg's Uncertainty Principle

«It is impossible to design an apparatus to determine which of two alternatives is taken without destroying the interference pattern»

$$\Delta p \Delta x \geq h$$

Quantum physics vs classical physics

Summary of first principles:

(1) The probability of an event is $P=|\psi|^2$, where ψ is a complex number we call amplitude.

(2) If an event can take place in different ways, then $P=|\sum_i \psi_i|^2$.

(3) If an experiment is able of determining which alternative is taken, then $P=\sum_i P_i$.

Why?

We only talk about predicting odds

Seems to explain everything on atomic scale

Quantum physics vs classical physics

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Schrödinger's Equation

1900-1926 – The years of confusion

$$E = h\nu$$

Planck's equation

$$p = \frac{h}{\lambda}$$

De Broglie's hypothesis

$$\Delta p \Delta x \geq h$$

Heisenberg's uncertainty

1927 – Postulate of the differential equation

Newton's 2nd law
- particles -

$$\vec{F} = \frac{d\vec{p}}{dt}$$

$$\frac{\partial^2 \Psi}{\partial t^2} = v^2 \frac{\partial^2 \Psi}{\partial x^2}$$

Wave equation
- waves -

$$\Psi(x, t) = A e^{i(kx - \omega t)} \longrightarrow \Psi(x, t) = A e^{i(px - Et)/\hbar}$$

$$k = \frac{2\pi}{\lambda}$$

$$\omega = 2\pi\nu$$

let's make it
dual

$$p = \hbar k$$

$$E = \hbar \omega$$

$$(\hbar = h/2\pi)$$

Schrödinger's Equation

Newton's 2nd law
- particles -

$$\vec{F} = \frac{d\vec{p}}{dt}$$

$$\frac{\partial^2 \Psi}{\partial t^2} = v^2 \frac{\partial^2 \Psi}{\partial x^2}$$

Wave equation
- waves -

$$\Psi(x, t) = A e^{i(px - Et)/\hbar} \longrightarrow \frac{E^2}{\hbar^2} \Psi = v^2 \frac{p^2}{\hbar^2} \Psi$$

Relativistic particles: $\begin{cases} v = c \\ E = pc \end{cases}$



Slow particles: $\begin{cases} v < c \\ \bar{E} = p^2/2m \end{cases}$



Guess: $\alpha \frac{\partial \Psi}{\partial t} = \beta \frac{\partial^2 \Psi}{\partial x^2} \longrightarrow i\hbar \frac{-i}{\hbar} E \Psi = \frac{-\hbar^2}{2m} \left(\frac{-p^2}{\hbar^2} \right) \Psi$

Schrödinger's Equation

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

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

Physical-mathematical considerations:

1) $\psi(\mathbf{r}, t)$ is the (complex) amplitude associated with the probability of finding a particle at (\mathbf{r}, t) . Call it *wave function*:

$$P(\vec{r}, t) = \Psi(\vec{r}, t)^* \Psi(\vec{r}, t)$$

2) Total probability of finding the particle confined in a volume must be unity.

$$\int \Psi(\vec{r}, t)^* \Psi(\vec{r}, t) dV = 1 \quad \text{normalization condition}$$

Then, $\psi(\mathbf{r}, t)$ must be square integrable. For bound particles, if $r \rightarrow \infty$ then $\psi(\mathbf{r}, t) \rightarrow 0$.

3) $\psi(\mathbf{r}, t)$ must be well behaved.

3.1) Finite.

3.2) Single-valued.

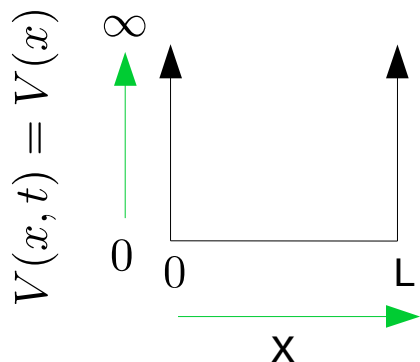
3.3) Continuous. 1st derivatives too.

4) Trivial solution, meaningless.

Let's play!

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

Particle in a 1D box



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

$$\Psi(x, t) = f(x) g(t)$$

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] f(x) = E f(x)$$

Time-independent
Schrödinger Equation
- stationary states -

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} f(x) = E f(x) \longrightarrow f(x) = A \sin kx + B \cos kx$$

Boundary conditions $\left\{ \begin{array}{l} f(0) = 0 \\ f(L) = 0 \end{array} \right.$

$f(0) = 0 \longrightarrow f(x) = A \sin kx$

$f(L) = 0 \longrightarrow 0 = \sin kL \longrightarrow k = \frac{\pi n}{L}, \quad n = 1, 2, 3 \dots$

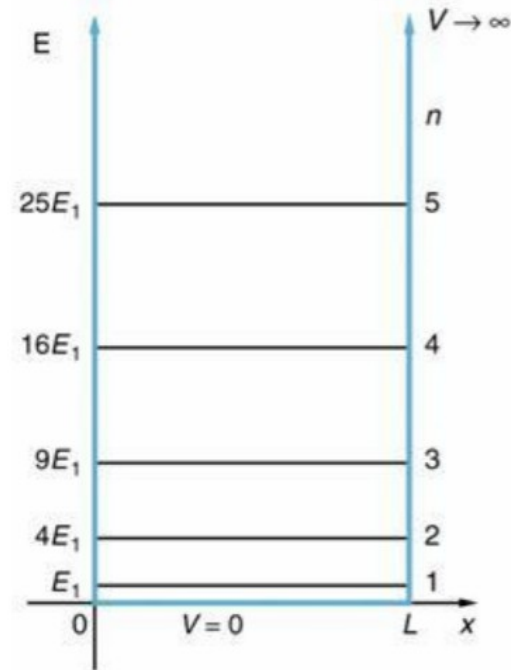
$$f_n(x) = A \sin \frac{n\pi x}{L}$$

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2$$

It's a quantum world

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

Energy is quantised



Quantised energies explain discrete atomic spectra:



H Balmer series, 1885

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2$$

Operators

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

Classical physics:
$$E = \frac{p^2}{2m} + V$$

Rule to move from classical to quantum

$$\left\{ \begin{array}{l} \hat{E} = i\hbar \frac{\partial}{\partial t} \quad \hat{p} = -i\hbar \nabla \quad \hat{V} = V. \\ \hat{x} = x \cdot \quad \hat{H} = \frac{\hat{p}^2}{2m} + \hat{V} \end{array} \right.$$

All operators are Hermitian

Remember: *We only talk about predicting odds*

Mean value of a physical magnitude:
$$\langle A \rangle = \frac{\int \Psi^* \hat{A} \Psi dV}{\int \Psi^* \Psi dV}$$



Schrödinger Equation

$$\hat{E}\Psi = \hat{H}\Psi$$

Variational principle

Let ψ be the eigenfunction of the Hamiltonian, with eigenvalue E_{exact} .

For any function Φ with the same boundary conditions, and well-behaved, it holds:

$$\langle E \rangle_{\text{approx}} = \frac{\int \Phi^* \hat{H} \Phi dV}{\int \Phi^* \Phi dV} \geq \frac{\int \Psi^* \hat{H} \Psi dV}{\int \Psi^* \Psi dV} = \langle E \rangle_{\text{exact}}$$

It is customary to build a basis set formed by linearly independent functions:

$\{\varphi_1, \varphi_2, \varphi_3 \dots\}$ whose scalar product is given by $\int \varphi_i^* \varphi_j dV$, define an

approximate solution as $\Phi = \sum_i c_i \varphi_i$ and obtain the coefficients by

minimizing $\langle E \rangle_{\text{approx}}$

Optimizing the basis set to reduce the required [Hilbert space](#) dimension has been the front line of Quantum Chemistry research for over 40 years now.

Quantum Physics and Mathematics:



- (*) Linear algebra
- (*) Algebra of creation/annihilation operators
- (*) Numerical methods
- (*) Group theory (symmetry and permutation groups)

What makes Quantum Physics different from earlier Physics?

- (1) Dual character particle-wave
- (2) No longer «deterministic». We calculate probable values
- (3) Simultaneous knowledge of some magnitudes impossible
- (4) Schrödinger equation replaces Newton 2nd law & wave eq.
- (5) Physical magnitudes have quantised values

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Variational Quantum Montecarlo

Let ψ be the eigenfunction of the Hamiltonian, with eigenvalue E_{exact} .

For any function Φ with the same boundary conditions, and well-behaved, it holds:

$$\langle E \rangle_{\text{approx}} = \frac{\int \Phi^* \hat{H} \Phi dV}{\int \Phi^* \Phi dV} \geq E_{\text{exact}}$$

We choose a trial function Φ_{α} with a set of adjustable parameters $\alpha = \{\alpha_1, \alpha_2, \alpha_3, \dots\}$, and look for those which minimize the energy.

An efficient way must be found to calculate the multi-dimensional integral above.

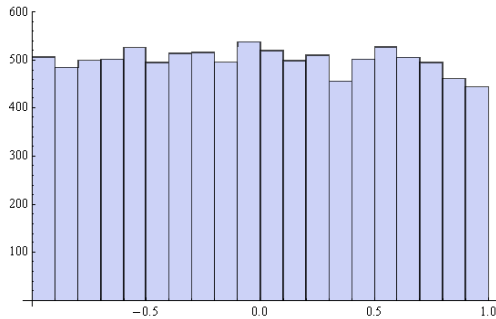
$$\begin{array}{l} \hat{H}\Psi(\vec{r}) = E\Psi(\vec{r}) \\ E_L(\vec{r}) = \frac{\hat{H}\Psi(\vec{r})}{\Psi(\vec{r})} \end{array} \left| \begin{array}{l} \longrightarrow \langle E \rangle_{\text{approx}} = \frac{\int |\Phi|^2 E_L dV}{\int |\Phi|^2 dV} \approx \frac{\sum |\Phi|^2 E_L dV}{\sum |\Phi|^2 dV} \\ \longleftarrow \end{array} \right.$$

Stochastic methods: draw random values within V , average integrand, minimize energy or variance

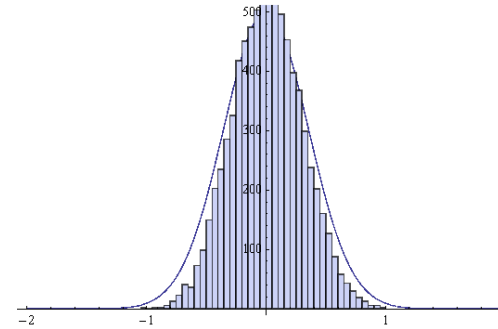
Variational Quantum Montecarlo

$$\langle E \rangle_{approx} = \frac{\sum |\Phi|^2 E_L dV}{\sum |\Phi|^2 dV} \quad E_L(\vec{r}) = \frac{\hat{H}\Phi(\vec{r})}{\Phi(\vec{r})}$$

Smart sampling critical for *efficient* calculation

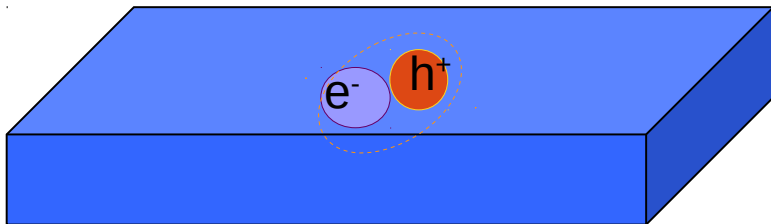


Random sampling (between -1 and 1)



Metropolis algorithm: priority to points with largest $|\Phi|^2$ values. Good results with **much** fewer points.

Standard technique for many-electron systems, **but fails for charges of opposite sign.**



$$\hat{H} = \sum_{i=e,h} \frac{\vec{p}_i^2}{2m} + V(\vec{r}_e) + V(\vec{r}_h) - \frac{1}{\epsilon r_{eh}}$$

$$\Phi = \Phi_e(\vec{r}_e)\Phi_h(\vec{r}_h) e^{-ar_{eh}}$$