Non-relativistic quantum mechanics

$\left(\text{Mathematical model for the motion of } N \text{ particles} \right.$
$\left. \text{(electrons, nuclei, atoms) in physical space and time.} \right)$

QM falls short of this expectation. Strictly speaking, QM is a mathematical formalism that allows to make empirical predictions about such systems which are confirmed by experiments very well.

To what extend the idea of particles moving in space and time (also when we do not perform experiments or „observations" on them) is an ongoing debate since almost 100 years.

My take on this: Yes, that's what QM is about.

Pseudo-philosophical talk like „physics is about measurements and observations only" is non-sense.

QM of N interacting spin-less point particles:

(1) The state of the system at time $t \in \mathbb{R}$ is (completely) described by the wave-function

$$\psi(t, \cdot): \mathbb{R}^{3N} \to \mathbb{C} \quad , \text{ where}$$

$$\| \psi(t, \cdot) \|^2_{L^2(\mathbb{R}^{3N})} := \int |\psi(t, q)|^2 \, dq^{3N} = 1$$

$$\| \Psi(t, \cdot) \|_{L^2(\mathbb{R}^{3N})}^2 := \int_{\mathbb{R}^{3N}} |\Psi(t, q)|^2 \, dq^{3N} = 1$$

is assumed. The physical meaning of $\Psi(t, \cdot)$ is that $\varrho(t, q) := |\Psi(t, q)|^2$ is a probability density: The probability that the configuration $Q(t)$ is (or is found to be when someone measures) in a subset $\Lambda \subset \mathbb{R}^{3N}$ of config. space is given by

$$\text{Prob}\left(Q(t) \in \Lambda \right) = \mathbb{P}^{\Psi_t}(\Lambda) := \int_{\Lambda} |\Psi(t, q)|^2 \, dq^{3N}.$$

Thus, the wave-fct. $\Psi_t(\cdot) := \Psi(t, \cdot)$ defines a probability measure $\mathbb{P}^{\Psi_t}$ on configuration space.

Warning: The wave fct. does not provide a mass- or charge density. QM is about point-particles, not about smeared out „stuff".

(2) The dynamical law specifying the time-evolution of the state $\Psi(t, \cdot)$ is the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(t, q) = -\hbar^2 \sum_{j=1}^{N} \frac{1}{2m_j} \Delta_{q_j} \Psi(t, q) + V(q) \Psi(t, q)$$

$$=: (H\Psi)(t, q)$$

where the linear operator   (to be defined on suitable fct. spaces)

$$H := -\hbar^2 \sum_{j=1}^{N} \frac{1}{2m_j} \Delta \dots V(q)$$

$$H := -\hbar^2 \sum_{j=1}^{N} \frac{1}{2m_j} \Delta_{q_j} + V(q)$$

is called the <u>Hamiltonian</u>. (comp. to Hamiltonian

fct $H(q,p) = \sum_{j=1}^{N} \frac{\|p_j\|^2}{2m_j} + V(q)$)

The Schrödinger equation is a linear partial differential equation (PDE) for a function on configuration space $\mathbb{R}^{3N}$.

<u>Stationary states</u>: Square integrable solutions of the <u>time-independent Schrödinger equation</u>

$$\boxed{(H \psi_E)(q) = E \psi_E(q)} \qquad \text{for some } E \in \mathbb{R}$$

are called <u>eigenstates</u> of H (or energy eigenstates),

and $\psi(t,q) := e^{-itE} \psi_E(q)$ is a <u>stationary solution</u> of the time-dependent SE.

Typically, only for a discrete set $\{E_j\} \subset \mathbb{R}$

L^2-solutions of the tiSE exist.

<u>Example</u>: • <u>free particle in a box</u> :

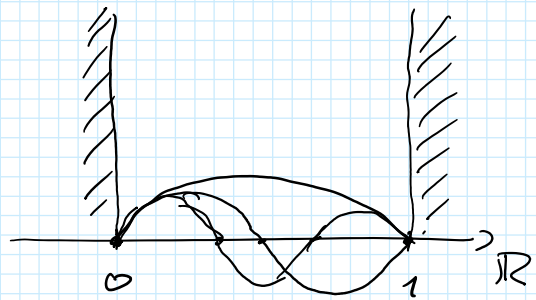$$-\frac{d^2}{dx^2} \psi(x) = E \psi(x) \qquad \text{for } \psi \in L^2([0,1])$$

with Dirichlet boundary conditions $\psi(0) = \psi(1) = 0$

$\longrightarrow \psi(x) := \sin(n \pi x) \sqrt{2}, \quad n \in \mathbb{N}$
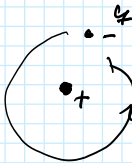
$\Rightarrow \psi_n(x) := \sin(n \cdot \pi x) \sqrt{2}$, $n \in \mathbb{N}$

with $E_n = n^2 \cdot \pi^2$
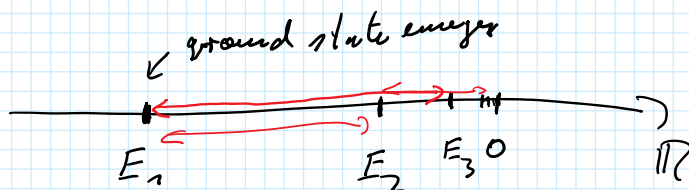
are the „energy eigenstates."

- **hydrogen atom:**

$H = -\frac{1}{2m_e} \Delta_q - \frac{C}{|q|}$ on $L^2(\mathbb{R}^3)$
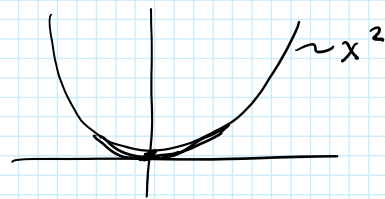
$\Rightarrow E_n = -\frac{\tilde{c}}{n^2}$,

for $n \in \mathbb{N}$

differences $E_n - E_m$ correspond to energies of spectral lines of hydrogen atoms, i.e. to photons absorbed or emitted by hydrogen. The corresponding eigenfcts. are called <u>orbitals</u>.

- **harmonic oscillator**

$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{m}{2} \omega^2 x^2$

$H \psi_n = E_n \psi_n$ for $E_n = \hbar \omega (n + \frac{1}{2})$ $n \in \mathbb{N}_0$

and $\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi \hbar} \right)^{1/4} H_n\left(\sqrt{\frac{m\omega}{\hbar}} \cdot x \right) e^{-\frac{m\omega x^2}{2\hbar}}$

Hermite polynomials

„<u>Axiomatic</u>" <u>formulation</u> of the quantum measurement formalism:

1.) **State space**: The possible states of a quantum system are described by normalised vectors $\psi \in \mathcal{H}$ in a Hilbert space $\mathcal{H}$.

2.) **Observables and operators**: Every physical observable A corresponds to a self-adjoint operator $\hat{A}$ on $\mathcal{H}$.

3.) **Measurement process**:

a) **Possible outcomes**: The measurement of an observable A yields as an outcome one of the eigenvalues of the corresponding operator $\hat{A}$.

b) **Probabilities**:

Let A be an observable and a_i an eigenvalue of the associated operator $\hat{A}$ and P_{a_i} the spectral projection on the corresp. eigenspace.

The probability for obtaining the result a_i when measuring the observable A on a system in the state ψ is

$$\text{Prob}(A = a_i \mid \psi) = \| P_{a_i} \psi \|^2 .$$

c) **State after the measurement**:

If the measurement of the observ. A on a quantum system in the state ψ yield the outcome a_i, then after the measurement the state of the system is

$$\psi_{\ldots} = \frac{P_{a_i} \psi}{\ldots}$$

$$\Psi_{coll.} = \frac{P_{a_i} \Psi}{\| P_{a_i} \Psi \|}$$

"collapse of the wave fct."

4) **Dynamical law:**

In between measurements the state Ψ of a system evolves according the Schrödinger equation

$$i\hbar \frac{d}{dt} \Psi(t) = \hat{H} \Psi(t) ,$$

where $\hat{H}$ is the Hamilton operator (the operator corresponding to the „energy" observable)

5.) **Correspondence principle:**

Let $A : \mathbb{R}^{6N} \to \mathbb{R}$, $(q,p) \mapsto A(q,p)$ be a classical observable. The corresponding operator $\hat{A}$ is

$$\hat{A} = A(q, -i\hbar \nabla_q)$$

acting on $L^2(\mathbb{R}^{3N}) = \mathcal{H}$.

Example: $\hat{H} = H(q, -i\hbar \nabla_q) = -\hbar^2 \sum_{j=1}^{N} \frac{1}{2m_j} \Delta_{q_j} + V(q)$

$\hat{p}_j = -i\hbar \nabla_{q_j}$ (momentum op.)

$\hat{q}_j = q_j$ (position op.)

$[\hat{q}_j, \hat{p}_i] = i\hbar \delta_{ij} = i\hbar \{q_j, p_i\}$

Dirac notation:

- vector $\Psi \in \mathcal{H}$ we written as $|\Psi\rangle$ („ket")

- the linear functional $\mathcal{J}_\Psi : \mathcal{H} \to \mathbb{C}$, $\varphi \mapsto \mathcal{J}_\Psi(\varphi) := \langle \Psi, \varphi \rangle_{\mathcal{H}}$

is written as $\langle \Psi |$ ("bra")

- the inner product of $\Psi, \varphi \in \mathcal{H}$ then becomes

  "bracket"

  $$\langle \varphi | \Psi \rangle := \langle \varphi, \Psi \rangle_{\mathcal{H}}$$

- while "ket bra" is a rank one lin. op.

  $$|\Psi\rangle\langle\varphi| : \mathcal{H} \to \mathcal{H}, \quad x \mapsto |\Psi\rangle\langle\varphi| x := \langle \varphi, x \rangle_{\mathcal{H}} \cdot \Psi$$

  $$\left(|\Psi\rangle\underbrace{\langle\varphi|x\rangle}_{\in \mathbb{C}} = \langle\varphi|x\rangle |\Psi\rangle \right)$$

- a bounded lin. op. $\hat{A} \in \mathcal{L}(\mathcal{H})$ can be written in terms

  of an ONB (Ψ_j) as

  $$\hat{A} = \sum_{j,i=1}^{\infty} |\Psi_j\rangle\underbrace{\langle\Psi_j|\hat{A}|\Psi_i\rangle}_{:= \langle \Psi_j, \hat{A}\Psi_i\rangle_{\mathcal{H}}}\langle\Psi_i| \qquad \text{"matrix elements of } \hat{A}\text{"}$$

<u>Spin</u>: particles with "spin" are described by $\mathbb{C}^n$-valued
wave fct.:

- the w.f. for one particle with spin $\frac{m}{2}$ ($m \in \mathbb{N}_0$)

  $$\Psi : \mathbb{R}^3 \to \mathbb{C}^{m+1}$$

  (e.g. for electrons $m=1$, but for nuclei $m=0$ or $m>1$

  are possible)

- w.f. for N particles with spin $\frac{m}{2}$

  $$\Psi : \mathbb{R}^{3N} \to \mathbb{C}^{(m+1)^N}$$

  (e.g. 6 electrons of a carbon atom: $\Psi : \mathbb{R}^{18} \to \mathbb{C}^{64}$)

- <u>Pauli Hamiltonian</u> for $N=1$, $m=1$:

  ↙ Pauli matrices

- **Pauli Hamiltonian for $N=1$, $m=1$:**

$$H\Psi = \frac{1}{2m}\left(-i D_q + e A(q)\right)^2 \Psi - c \langle \sigma, B(q)\rangle_{\mathbb{R}^3} \Psi + V(q)\Psi$$

Pauli matrices

vector potential

$\in \mathcal{L}(\mathbb{C}^2)$

magnetic field

$B = \text{curl } A$

Identical particles: $\quad q = (q_1, .., q_N)$

- m even $\rightsquigarrow$ <u>bosons</u> $\rightsquigarrow$ $\Psi: \mathbb{R}^{3N} \to \mathbb{C}^{(m+1)^N}$

  symmetric under permutations of arguments,

  $$\Psi(q_{\pi(1)}, \ldots, q_{\pi(N)}) = U_\pi \Psi(q_1, \ldots q_N) \qquad \forall \pi \in S_N$$

- m odd $\rightsquigarrow$ <u>fermions</u> $\rightsquigarrow$ $\Psi: \mathbb{R}^{3N} \to \mathbb{C}^{(m+1)^N}$

  anti-symmetric under permutations of arguments

  $$\Psi(q_{\pi(1)}, \ldots, q_{\pi(N)}) = \text{sgn}(\pi)\, U_\pi \Psi(q_1, \ldots, q_N) \qquad \forall \pi \in S_N.$$