Non-relativistic quantum mechanics

We would hope for a mathematical model for the motion of N particles in small scales (electrons, nuclei, atoms, ...) in physical space and time. However, quantum mechanics fall short of this expectation. Strictly speaking, quantum mechanics is a mathematical formalism that allows making empirical predictions about such systems, which are confirmed by experiments very well. The physical nature of those particles moving in space and time (also when we do not perform experiments or "observations" on them) is an ongoing debate for almost 100 years.

Quantum mechanics 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*

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

where

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

is assumed. The physical meaning of $\psi(t, \cdot)$ is that

$$\rho(t, q) = |\psi(t, q)|^2$$

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 configuration space is given by

$$Prob(Q(t) \in \Lambda) = \mathbb{P}^{\psi_t}(\Lambda) = \int_\Lambda |\psi(t, q)|^2 \, d^{3N}q.$$

Thus, the wave-function $\psi_t(\cdot) = \psi(t, \cdot)$ defines a *probability measure* $\mathbb{P}^{\psi_t}$ on configuration space. It should be noted that the wave function does

not provide a mass- or charge density. Quantum mechanics 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*

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

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

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

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

Definition 8.1 (Definition). Square integrable solutions of the time-independent Schrödinger equation

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

are called *eigenstates* of H (or energy eigenstates), and

$$\psi(t,q) = e^{-itE}\psi_E(q)$$

is a *stationary solution* of the time-dependent Schrödinger equation.
Typically, only for a discrete set $\{E_j\} \subset \mathbb{R}$ solutions of the time-independent Schrödinger equation in L^2 exist.

Example 8.2.   1. Free particle in a box:

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

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

$$\Rightarrow \psi_n(x) = \sqrt{2}\sin(n\cdot\pi\cdot x) \qquad n \in \mathbb{N}$$

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

2. Hydrogen atom:

$$H = -\frac{1}{2m_e}\Delta_q - \frac{c}{|q|} \qquad \text{on } L^2(\mathbb{R}^3)$$

with the energy eigenstates of $E_n = -\frac{\tilde{c}}{n^2}$ for $n \in \mathbb{N}$. The 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 eigenfunctions are called *orbitals*.

3. Harmonic oscillator:

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

For the time-independent Schrödinger equation

$$H\psi_n = E_n\psi_n \quad \text{one gets} \quad E_n = \hbar\omega\left(n + \frac{1}{2}\right) \quad n \in \mathbb{N}_0$$

and

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

with $H_n(\cdot)$ being the Hermite polynomials.

"Axiomatic" formulation 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 corresponding eigenspace. The probability for obtaining the result a_i when measuring the observable A on a system in the state ψ is

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

   (c) *State after the measurement:* If the measurement of the observable A on a quantum system in the state ψ yields the outcome a_i, then after the measurement the state of the system is

   $$\psi_{coll.} = \frac{P_{a_i}\psi}{\|P_{a_i}\psi\|}$$

   "collapse of the wave function".

4. *Dynamic law:* In between measurements the state ψ of the system evolves according to 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 $A : \mathbb{R}^{6N} \to \mathbb{R}, \quad (q, p) \mapsto A(q, p)$ be a classical observable. Then the corresponding operator $\hat{A}$ is the given

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

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

Example 8.3 (Examples of the applied correspondence principle)**.**

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

2. $\hat{p}_j = -i\hbar\nabla_{q_j}$ the momentum operator

3. $\hat{q}_j = q_j$ the position operator

4. $[\hat{q}_j, \hat{p}_i] = i\hbar\delta_{ij} \leftrightarrow \{q_j, p_j\} = \delta_{ij}$, i.e. the Poisson bracket of classical mechanics is replaced by the commutator.

Remark 8.4 (Dirac notation). It has turned out to be quite advantageous in the context of quantum mechanics to use the notation of Paul Dirac (1902 - 1984).

1. Vectors $\psi \in \mathcal{H}$ are written as $|\psi\rangle$ ("ket")

2. The linear functional $J_\psi : \mathcal{H} \to \mathbb{C}, \quad \varphi \mapsto J_\psi(\phi) = \langle\psi|\varphi\rangle_\mathcal{H}$ is written as $\langle\psi|$ ("bra")

3. The inner product of $\psi, \varphi \in \mathcal{H}$ then becomes:

$$\langle\varphi|\psi\rangle = \langle\varphi|\psi\rangle_\mathcal{H}$$

4. while "ket bra" is a rank one operator:

$$|\psi\rangle\langle\varphi| : \mathcal{H} \to \mathcal{H}, \quad \chi \mapsto |\psi\rangle\langle\varphi|\,\chi = \langle\varphi|\chi\rangle_\mathcal{H}\,\psi\,.$$

5. A bounded linear operator $\hat{A} \in \mathcal{L}(\mathcal{H})$ can be written in terms of an ONB (ψ_j) as

$$\hat{A} = \sum_{j,i=1}^{\infty} |\psi_j\rangle \left\langle\psi_j\middle|\hat{A}\psi_i\right\rangle \langle\psi_i| = \sum_{ij} \left\langle\psi_j\middle|\hat{A}\psi_i\right\rangle |\psi_j\rangle\langle\psi_i|\,.$$

Definition 8.5 (Spin)**.** Particles with "spin" are described by $\mathbb{C}^n$-valued wave functions:

1. The wave function for one particle with spin $\frac{m}{2}$ ($m \in \mathbb{N}_0$)

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

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

2. wave function 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: $\psi : \mathbb{R}^{18} \to \mathbb{C}^{64}$).

3. The Pauli Hamiltonian for $N = 1$, $m = 1$ is given by

$$H\psi = \frac{1}{2m} \left(-i\nabla_q + eA(q)\right)^2 \psi - c \underbrace{\langle \sigma | B(q) \rangle_{\mathbb{R}^3}}_{\in \mathcal{L}(\mathbb{C}^2)} \psi,$$

with σ being Pauli matrices, $A(q)$ the vector potential and $B(q)$ the magnetic field ($B = \operatorname{curl} A$).

Definition 8.6 (Bosonic and fermionic wave functions)**.** Let us consider N identical particles, i.e. $q = (q_1, \ldots, q_N)$. We then distinguish two cases.

1. m even $\to$ bosons $\to \psi : \mathbb{R}^{3N} \to \mathbb{C}^{(m+1)^N}$ symmetric under permutation of arguments,

$$\psi(q_{\pi(1)}, \ldots, q_{\pi(n)}) = U_\pi \psi(q_1, \ldots, q_N) \quad \forall \pi \in S_N$$

2. m odd $\to$ fermions $\to \psi : \mathbb{R}^{3N} \to \mathbb{C}^{(m+1)^N}$ anti-symmetric under permutation of arguments

$$\psi(q_{\pi(1)}, \ldots, q_{\pi(N)}) = sgn(\pi) U_\pi \psi(q_1, \ldots, q_N) \quad \forall \pi \in S_N$$

Exercises

1. Define the angular momentum operator in direction z by

$$\hat{L}_z \doteq \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \,.$$

Use the canonical commutation relation to show that

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\,\epsilon_{xyz}\hat{L}_z \,.$$

2. Let $\psi \in C^\infty\big([0,T],\mathcal{H}\big)$ be a solution to the Schrödinger equation. Show that if $\|\psi(0)\| = 1$, then $\|\psi(t)\| = 1$ for all $t \in [0,T]$.

3. We consider the Hilbert space of a "qubit" $\mathcal{H} = \mathbb{C}^2$.

(a) What are the possible outcomes and their respective probabilities when measuring the state $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ with respect to the operator $\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ (spin in y-direction). What is the state of the system after the measurement in either case?

(b) Suppose the state is now given by $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix} = \psi_0$ and evolves according to the Schrödinger equation with respect to $H = B\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$, where $B > 0$, for a time T and then is measured with respect to $\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$. What are the probabilities of the possible outcomes.

(c) Consider the state $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$. Compare measuring it with respect to $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ with measuring first with respect to $\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ and then $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$.