

UNTERNEHMEN TAIFUN

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Part I

Fundamentals

Chapter 1

Quantum Mechanics

Hierzu ist es notwendig, die Energy nicht als eine stetige unbeschränkt teilbare, sondern als eine discrete, aus einer ganzen Zahl von endlichen gleichen Teilen zusammengesetzte Grösse aufzufassen.

— Max Planck

1.1 Classical Mechanics

The formalism used in quantum mechanics largely stems from William Rowan Hamilton's formulation of classical mechanics. Through the process of canonical quantisation any classical model of a physical system is turned into a quantum mechanical model.

In Hamilton's formulation of classical mechanics, a complete description of a system of N particles is described by a set of canonical coordinates $q = (\vec{q}_1, \dots, \vec{q}_N)$ and corresponding conjugate momenta $p = (\vec{p}_1, \dots, \vec{p}_N)$. Together, each pair of coordinate and momentum form a point $\xi = (q, p)$ in phase space, which is a space of all possible states of the system. Moreover, pairs of generalised coordinates and conjugate momenta are canonical if they satisfy the Poisson brackets so that $\{q_i, p_k\} = \delta_{ij}$. The Poisson bracket of two functions is defined as

$$\{f, g\} = \frac{\partial f}{\partial q} \frac{\partial g}{\partial p} - \frac{\partial f}{\partial p} \frac{\partial g}{\partial q}. \quad (1.1)$$

The governing equations of motion in a classical system is Hamilton's equations,

$$\dot{q} = \frac{\partial}{\partial p} \mathcal{H}(q, p) \quad (1.2)$$

$$\dot{p} = -\frac{\partial}{\partial q} \mathcal{H}(q, p) \quad (1.3)$$

where $\mathcal{H}(q, p)$ is the Hamiltonian, a function for the total energy of the system. Hamilton's equations may also be stated in terms of the Poisson brackets,

$$\frac{dp_i}{dt} = \{p_i, \mathcal{H}\}, \quad \frac{dq_i}{dt} = \{q_i, \mathcal{H}\}. \quad (1.4)$$

A system consisting of N of equal mass m , subject forces caused by an external potential, as well as acting on each other with forces stemming from a central potential $w(q_{ij})$ has the following Hamiltonian,

$$\mathcal{H}(q, p) = \mathcal{T}(q) + \mathcal{V}(p) + \mathcal{W}(p) = \frac{1}{2m} \sum_i |\vec{p}_i|^2 + \sum_i v(\vec{r}_i) + \frac{1}{2} \sum_{i < j} w(r_{ij}). \quad (1.5)$$

This Hamiltonian conveniently contains several parts - the kinetic energy, the external potential energy and the interaction energy; denoted by \mathcal{T} , \mathcal{V} and \mathcal{W} respectively.

1.2 Canonical Quantisation

In order to transition from a classical system to a quantum system, we move from the classical phase space to the Hilbert space, through the procedure known as canonical, or first¹-, quantisation. Whilst the state of a classical system is a point in phase space, a quantum state is a complex-valued state vector in discrete, infinite dimensional, Hilbert space, that is a complete vector space equipped with an inner product. This space is most commonly chosen to be the space of square-integrable functions Ψ , dependent on all coordinates

$$\Psi = \Psi(x_1, x_2, \dots, x_N). \quad (1.6)$$

These functions are dubbed wavefunctions and are maps from a point (x_1, \dots, x_N) in configuration space to the complex vector space,

$$\Psi : X^N \rightarrow \mathbb{C}. \quad (1.7)$$

It has been widely discussed how such an object can represent the state of a particle. The answer is provided by Max Born's probabilistic interpretation, which says that $|\Psi(x_1, \dots, x_N)|^2$, gives the probability of finding the particle at a certain position. For a situation with one particle in one dimension we have,

$$\int_a^b |\Psi(x)|^2 dx = \left\{ \begin{array}{l} \text{probability of finding the} \\ \text{particle between } a \text{ and } b \end{array} \right\} \quad (1.8)$$

while $|\Psi(x_1, x_2, \dots, x_N)|^2$ is the probability density for locating all particles at the point $(x_1, \dots, x_N) \in X^N$. Since the total probability must be 1, we are provided with a normalisation condition for the wavefunction,

$$\int_{X^N} |\Psi(x_1, x_2, \dots, x_N)|^2 dx_1 dx_2 \dots dx_N = 1. \quad (1.9)$$

1.2.1 The Dirac-von Neumann Postulates

The following postulates, or axioms, provide a precise and concise description of quantum mechanics in terms of operators on the Hilbert space. There are many variations of these postulates, introduced both by their namesakes Paul Adriene Maurice Dirac[1] and John von Neumann[2].

Hilbert Space A quantum state of an isolated physical system is described by a vector with unit norm in a Hilbert space, a complex vector space equipped with a scalar product.

¹Second quantisation comes later.

Observables Each physical observable of a system is associated with a *hermitian* operator acting on the Hilbert space. The eigenstates of each such operator define a *complete, orthonormal* set of vectors.

With \hat{O} an operator, hermiticity means,

$$\langle \phi | \hat{O} \psi \rangle = \langle \hat{O} \phi | \psi \rangle \equiv \langle \phi | \hat{O} | \psi \rangle. \quad (1.10)$$

Completeness means,

$$\sum_i |i\rangle \langle i| = \mathbf{1}. \quad (1.11)$$

Orthonormal means,

$$\langle i | j \rangle = \delta_{ij}. \quad (1.12)$$

Time Evolution The time evolution of the state vector, $|\psi\rangle = |\psi(t)\rangle$, is given by the Schrödinger equation².

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle. \quad (1.13)$$

Measurements Physically measurable values, associated with an observable \hat{O} are defined by the eigenvalues o_n of the observable,

$$\hat{O} |n\rangle = o_n |n\rangle. \quad (1.14)$$

The probability for finding a particular eigenvalue in the measurement is

$$p_n = |\langle n | \psi \rangle|^2, \quad (1.15)$$

with the system in state $|\psi\rangle$ before the measurement, and $|n\rangle$ as the eigenstate corresponding to the eigenvalue o_n .

1.3 The Many-Body Quantum Hamiltonian

The full Hamiltonian for a quantum many-body system can be a large and unwieldy thing.

Free particle in one dimension,

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (1.16)$$

Introduce potential.

Many particles in many dimensions.

Interaction.

Nuclear interaction (molecule).

There is other stuff as well.

1.3.1 Born-Oppenheimer

1.4 Indistinguishable Particles

In a quantum system the particles are identical and impossible to tell apart, as indicated by several studies (KILDE!!). The probability density for the location of particles in a system must therefore be permutation invariant,

²In the Schrödinger picture.

$$|\Psi(x_1, x_2, \dots, x_i, x_j x_N)|^2 = |\Psi(x_1, x_2, \dots, x_j, x_i x_N)|^2. \quad (1.17)$$

For any arbitrary permutation, this is equivalent to

$$\Psi(x_1, \dots, x_N) = e^{i\alpha(\sigma)} \Psi(x_{\sigma(1)}, x_{\sigma(2)}, \dots, x_{\sigma(N)}), \quad (1.18)$$

where $\sigma \in S_N$ is some permutation of N indices and α is some real number that may be dependent on σ .

The same relation can be written by way of a linear permutation operator,

$$(\hat{P}_\sigma \Psi)(x_1, \dots, x_N) = \Psi(x_{\sigma(1)}, x_{\sigma(2)}, \dots, x_{\sigma(N)}). \quad (1.19)$$

1.4.1 Slater Determinants