# Unternehmen Taifun

by

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# Part I

# Fundamentals

# Chapter 1

# Quantum Mechanics

## 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 $q = (\vec{q}_1, \ldots, \vec{p}_N)$ and corresponding conjugate momenta $p = (\vec{p}_1, \ldots \vec{p}_N)$. 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

$$\{f, g\} = \frac{\partial f}{\partial q} \frac{\partial g}{\partial g} - \frac{\partial f}{\partial p} \frac{\partial g}{\partial q}. \tag{1.1}$$

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

$$\dot{q} = \frac{\partial}{\partial p} \mathscr{H}(q, p) \tag{1.2}$$

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

where $\mathscr{H}(q, p)$ 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,

$$\frac{dp_i}{dt} = \{p_i, \mathscr{H}\}, \ \frac{dq_i}{dt} = \{q_i, \mathscr{H}\}. \tag{1.4}$$

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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 potetntial $w(q_i j)$ has the following Hamiltonian,

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

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

## 1.2  Canonical Quantisation

In order to transition from a classical system to a quantum system, we move from the classucal phase space to the Hilbert space, through the procedure known as canonical, or first[1]-, 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 $\Psi$, dependent on all coordinates

$$\Psi = \Psi(x_1, x_2, \ldots, x_N). \qquad (1.6)$$

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

$$\Psi : X^N \to \mathbb{C}. \qquad (1.7)$$

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 $|\Psi(x_1, \ldots, x_N)|^2$, gives the probability of finding the particle at a certain position. For a situation with one particle in one dimension we have,

$$\int_a^b |\Psi(x)|^2 dx = \begin{Bmatrix} \text{probability of finding the} \\ \text{particle between } a \text{ and } b \end{Bmatrix} \qquad (1.8)$$

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

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

### 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 quipped with a scalar product.

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[1]Second quantisation comes later.

**Observables**  Each physical observable of a system is accociated 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,

$$\langle\phi|\,\hat{O}\psi\rangle = \langle\hat{O}\phi\,|\psi\rangle \equiv \langle\phi|\,\hat{O}\,|\psi\rangle. \tag{1.10}$$

Completeness means,

$$\sum_i |i\rangle\,\langle i| = \mathbb{1}. \tag{1.11}$$

Orthonormal means,

$$\langle i|j\rangle = \delta_{ij}. \tag{1.12}$$

**Time Evolution**  The time evolution of the state vector, $|\psi\rangle = |\psi(t)\rangle$, is given by the Schrödinger equation[2].

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

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

$$\hat{O}\,|n\rangle = o_n\,|n\rangle. \tag{1.14}$$

The probability for finding a particular eigenvalue in the measurement is

$$p_n = |\langle n|\psi\rangle|^2, \tag{1.15}$$

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 Hamiltionian for a quantum many-body system can be a large and unwieldy thing. In this study we will constrain ourselves to the study of electronic systems. Electronic systems are

Free particle in one dimension,

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

Introduce potential.
Many particles in many dimenions.
Interaction.
Nuclear interaction (molecule).
There is other stuff as well.
In atomic units, the Hamiltonian for $N$ electrons and $M$ nuclei is [3],

$$\hat{H} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}}, \tag{1.17}$$

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[2]In the Schrödinger picture.
[3]Often referred to as the electronic Hamiltonian

Table 1.1: Conversion of atomic units to SI units THIS IS FROM SZABO AND OSTLUND.

| Physical quantity | Conversion factor | Value |
|---|---|---|
| Length | $a_0$ | $5.2918 \times 10^{-11} m$ |
| Mass | $m_e$ | $9.1095 \times 10^{-31} kg$ |
| Charge | $e$ | $1.6022 \times 10^{-19} C$ |
| Energy | $E_a$ | $4.3598 \times 10^{-18} J$ |
| Angular momentum | $\hbar$ | $1.0546 \times 10^{-34} Js$ |
| Electric dipole moment | $ea_0$ | $8.4784 \times 10^{-30} Cm$ |
| Electric polarizability | $e^2 a_0^2 / E_a$ | $1.6488 \times 10^{-41} C^2 m^2 J^{-1}$ |
| Electric field | $E_a/(ea_0)$ | $5.1423 \times 10^{11} V m^{-1}$ |
| Wave function | $a_0^{-3/2}$ | $2.5978 \times 10^{15} m^{-3/2}$ |

where $M_A$ si the ratio of the mass of nucleus $A$ to the mass of an electron, and $Z_A$ is the atomic number of nuclus $A$. The first term in Equation 1.17 is the operator for the kinetic energy of the electrons, the second term is the operator for the kinetic energi of the nuclei, the third term represents the Coulomb attraction between the electrons and the nuclei, the fourth term is the Coulomb repulsion between electrons and the fifth and last term is the Coulomb repulsion between nuclei.

PERHAPS FIGURE OF GENERAL SYSTEM HERE?

### 1.3.1   Atomic Units

In the Hamiltionian above (Equation 1.17), we have grown up and set $\hbar = m_e = e = \cdots = 1$. This is a result of using atomic units, a form of commonly used dimensionless units. To see how these units arise, consider the time-independent Schrödinger equation for a Hydrogen atom,

$$\left( -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) \phi = E\phi, \tag{1.18}$$

where $\hbar$ is the reduced Planck constant, equal to Planck's constant divided by $2\pi$; $m_e$ is the mass of the electron, $-e$ is the charge of the electron and $\epsilon_0$ is the permitivity of free space. We make this equation dimensionless by letting $r \to \lambda r'$,

$$\left( -\frac{\hbar^2}{2m_e\lambda^2}\nabla'^2 - \frac{e^2}{4\pi\epsilon_0 \lambda r'} \right) \phi' = E\phi'. \tag{1.19}$$

We can factor out the constants in front of the operators, if we choose $\lambda$ so that,

$$\frac{\hbar^2}{m_e\lambda^2} = \frac{e^2}{4\pi\epsilon_0\lambda} = E_a \to \lambda\frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = a_0 \tag{1.20}$$

where $E_a$ is the atomic unit of energy that chemists call Hartree. Incidently, we see that $\lambda$ is just the Bohr radius, $a_0$. If we let $E' = E/E_a$, we obtain the dimensionless Schrödinger equation,

$$\left( -\frac{1}{2}\nabla'^2 - \frac{1}{r'} \right) \phi' = E'\phi'. \tag{1.21}$$

Some conversion factors between atomic units and SI units can be found in Table 1.1.

### 1.3.2  The Born-Oppenheimer Approximation

## 1.4  Indistinguishable Particles

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

$$|\Psi(x_1, x_2, \ldots, x_i, x_j x_N)|^2 = |\Psi(x_1, x_2, \ldots, x_j, x_i x_N)|^2. \tag{1.22}$$

For any arbitrary permutation, this is equivalent to

$$\Psi(x_1, \ldots x_N) = e^{i\alpha(\sigma)} \Psi(x_{\sigma(1)}, x_{\sigma(2)}, \ldots, x_{\sigma(N)}), \tag{1.23}$$

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

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

$$(\hat{P}_\sigma \Psi)(x_1, \ldots, x_N) = \Psi(x_{\sigma(1)}, x_{\sigma(2)}, \ldots, x_{\sigma(N)}). \tag{1.24}$$

### 1.4.1  Slater Determinants

# Bibliography

[1]  Paul Adrien Maurice Dirac. *The Principles of Quantum Mechanics.* Oxford University Press, 1930.

[2]  John von Neumann. *Mathematical Foundations of Quantum Mechanics.* Berlin: Springer, 1932.