

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. In this study we will constrain ourselves to the study of electronic systems. Electronic systems are

Free particle in one dimension,

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

Introduce potential.

Many particles in many dimensions.

Interaction.

Nuclear interaction (molecule).

There is other stuff as well.

In atomic units, the Hamiltonian for N electrons and M nuclei is ³,

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

²In the Schrödinger picture.

³Often 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 | $E_a / (ea_0)$ | $5.1423 \times 10^{11} Vm^{-1}$ |
| Wave function | $a_0^{-3/2}$ | $2.5978 \times 10^{15} m^{-3/2}$ |

where M_A is the ratio of the mass of nucleus A to the mass of an electron, and Z_A is the atomic number of nucleus 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 energy 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 Hamiltonian above (Equation 1.17), we have grown up and set $\hbar = m_e = e = \dots = 1$. 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,

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

where \hbar is the reduced Planck constant, equal to Planck's constant divided by 2π ; m_e is the mass of the electron, $-e$ is the charge of the electron and ϵ_0 is the permittivity of free space. We make this equation dimensionless by letting $r \rightarrow \lambda r'$,

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

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

$$\frac{\hbar^2}{m_e \lambda^2} = \frac{e^2}{4\pi\epsilon_0 \lambda} = E_a \rightarrow \lambda \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = a_0 \quad (1.20)$$

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

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

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 and Pauli

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,

$$|\Psi(x_1, x_2, \dots, x_i, x_j x_N)|^2 = |\Psi(x_1, x_2, \dots, x_j, x_i x_N)|^2. \quad (1.22)$$

For any arbitrary permutation, this is equivalent to

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

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,

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

1.5 Representation of the Wavefunction

1.6 Orbitals

1.6.1 Hartree Products

1.6.2 Slater Determinants

1.7 The Harmonic Oscillator System

Chapter 2

Second Quantisation

Some Slater determinant is written,

$$|\Phi\rangle = |\phi_i \phi_j \phi_k \dots \phi_z\rangle = |ijk\dots z\rangle. \quad (2.1)$$

2.1 Creation and Annihilation Operators

I SHOULD PROBABLY CHANGE TO Qs HERE...?

The notation of creation and annihilation operators vary,

$$\begin{aligned} &\text{creation operator for spinorbital } \phi_i, \hat{X}_i^\dagger, \hat{a}_i^\dagger, \hat{c}_i^\dagger, \hat{i}^\dagger; \\ &\text{annihilation operator for spinorbital } \phi_i, \hat{X}_i, \hat{a}_i, \hat{c}_i, \hat{i}. \end{aligned}$$

Herein, \hat{a}_i^\dagger , \hat{a}_i is used and, if there is no change of confusion, \hat{i}^\dagger , \hat{i} .

The Creation Operator . For every single-particle index q , we define the creation operator c_q^\dagger acting on the vacuum state by

$$\hat{a}_i^\dagger |0\rangle = |q\rangle. \quad (2.2)$$

For any Slater determinant with $N > 0$, the action is defined by

$$\hat{a}_i^\dagger |ijk\dots z\rangle = |ijk\dots z\rangle, \quad (2.3)$$

$$\hat{a}_i^\dagger |ijk\dots z\rangle = 0 \quad (2.4)$$

The Annihilation Operator . It is sufficient to state that the annihilation c_i operator is the hermitian adjoint of the creation operator \hat{c}_i , but to specify we have

$$\hat{a}_i |0\rangle = 0, \quad (2.5)$$

as there is no particle in the vacuum state to annihilate.

For any arbitrary Slater determinant, we have

$$\hat{a}_i |ijk\dots z\rangle = |ij\dots z\rangle, \quad (2.6)$$

$$\hat{a}_i |ijk\dots z\rangle = 0 \quad (2.7)$$

SOMETHING MORE ABOUT THE DIFFERENT PERMUTATIONS.

We can now build a Slater determinant as the result of successive operation of several creation operators \hat{a}_q^\dagger on the vacuum state,

$$\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k^\dagger \dots \hat{a}_z^\dagger |0\rangle = |ijk\dots z\rangle. \quad (2.8)$$

It is convenient to arrange the spinorbitals in a Slater determinant in alphabetical order, as in Equation 2.8. This makes it necessary to ascertain the effects a creation or annihilation operator will have on a Slater determinant when the affected orbital is not at the beginning of the string of orbitals in the Slater determinant. Generally we have,

$$\hat{P} |ijk\dots z\rangle = (-1)^{\sigma(\hat{P})} |ijk\dots z\rangle, \quad (2.9)$$

where \hat{P} permutes the string of orbitals and $\sigma(\hat{P})$ is the parity of the permutation \hat{P} . we have

$$\hat{a}_p^\dagger |ijk\dots z\rangle = (-1)^{\eta_p} |ijk\dots p\dots z\rangle, \quad (2.10)$$

$$\hat{a}_p |ijk\dots p\dots z\rangle = (-1)^{\eta_p} |ijk\dots z\rangle, \quad (2.11)$$

where η_p is the number of orbitals preceeding the orbital ϕ_p , pertaining to the creation (annihilation) operator, in the Slater determinant.

2.2 Anticommutator Relations

Consider some creation operators acting on a Slater determinant,

$$\begin{aligned} \hat{a}_p^\dagger \hat{a}_q^\dagger |ijk\dots\rangle &= |pqijk\dots\rangle \\ \hat{a}_q^\dagger \hat{a}_p^\dagger |ijk\dots\rangle &= |qpijk\dots\rangle = -|pqijk\dots\rangle. \end{aligned} \quad (2.12)$$

We demand that these two operations be equivalent, or that

$$\begin{aligned} \hat{a}_p^\dagger \hat{a}_q^\dagger &= -\hat{a}_q^\dagger \hat{a}_p^\dagger \\ \{\hat{a}_p^\dagger, \hat{a}_q^\dagger\} &\equiv \hat{a}_p^\dagger \hat{a}_q^\dagger + \hat{a}_q^\dagger \hat{a}_p^\dagger = \hat{0}. \end{aligned} \quad (2.13)$$

This is one of several important anti-commutator relations for creation and annihilation operators.

Similarly, for annihilation operators we have

$$\begin{aligned} \hat{a}_p \hat{a}_q |qpijk\dots\rangle &= \hat{a}_p |pijk\dots\rangle = |ijk\dots\rangle \\ \hat{a}_q \hat{a}_p |qpijk\dots\rangle &= -\hat{a}_q \hat{a}_p |pqijk\dots\rangle = -\hat{a}_q |qijk\dots\rangle = -|ijk\dots\rangle. \end{aligned} \quad (2.14)$$

These two operations must also be equivalent,

$$\begin{aligned} \hat{a}_p \hat{a}_q &= -\hat{a}_q \hat{a}_p \\ \{\hat{a}_p, \hat{a}_q\} &\equiv \hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p = \hat{0}. \end{aligned} \quad (2.15)$$

One case remains, when a creation operator and an annihilation operator is applied together on a Slater determinant,

$$\hat{a}_p^\dagger \hat{a}_q |qijk\dots\rangle = \hat{a}_p^\dagger |ijk\dots\rangle = |pijk\dots\rangle. \quad (2.16)$$

This operation will replace ϕ_q by ϕ_p even if ϕ_p would have been somewhere else in the interior of the Slater determinant. Any sign change as an effect of moving the orbital to the front of the

string would be negated when the orbital is moved back to the original position. Exchanging the order of the operators however,

$$\hat{a}_q \hat{a}_p^\dagger |qijk \dots\rangle = \hat{a}_q |pqijk \dots\rangle = -\hat{a}_q |qpijk \dots\rangle = -|pijk \dots\rangle. \quad (2.17)$$

We again see a sign change and have,

$$\{\hat{a}_p^\dagger, \hat{a}_q\} = \hat{0} \quad (p \neq q). \quad (2.18)$$

If, on the other hand, $p = q$ we have

$$\begin{aligned} \hat{a}_p^\dagger \hat{a}_p |pijk \dots\rangle &= |pijk \dots\rangle, \\ \hat{a}_p \hat{a}_p^\dagger |pijk \dots\rangle &= 0, \end{aligned} \quad (2.19)$$

and if the orbital ϕ_p in question does not appear in the Slater determinant,

$$\begin{aligned} \hat{a}_p^\dagger \hat{a}_p |ijk \dots\rangle &= 0, \\ \hat{a}_p \hat{a}_p^\dagger |ijk \dots\rangle &= \hat{a}_p |pijk \dots\rangle = |ijk \dots\rangle. \end{aligned} \quad (2.20)$$

For all cases we have that,

$$(\hat{a}_p^\dagger \hat{a}_p + \hat{a}_p \hat{a}_p^\dagger) |\dots\rangle = |\dots\rangle, \quad (2.21)$$

or

$$\{\hat{a}_p^\dagger, \hat{a}_p\} = \{\hat{a}_p, \hat{a}_p^\dagger\} = \hat{1}. \quad (2.22)$$

In conclusion, the anti-commutator relations of the creation and annihilation operators are,

$$\{\hat{a}_p, \hat{a}_q\} = \hat{0}, \quad (2.23)$$

$$\{\hat{a}_p^\dagger, \hat{a}_q^\dagger\} = \hat{0}, \quad (2.24)$$

$$\{\hat{a}_p^\dagger, \hat{a}_q\} = \{\hat{a}_p, \hat{a}_q^\dagger\} = \delta_{pq}. \quad (2.25)$$

2.3 Representation of Operators

A second-quantised one-body operator is written like

$$\hat{h} = \sum_{i=1}^N \hat{h}(i) = \sum_{ij} \langle i | \hat{h} | j \rangle \hat{a}_i^\dagger \hat{a}_j, \quad (2.26)$$

where in general, $\langle p | \hat{h} | q \rangle$ is the matrix element of the single-particle operator \hat{h} in a given one-particle basis,

$$\langle p | \hat{h} | q \rangle = \int dx \phi_p(x)^* \hat{h} \phi_q(x). \quad (2.27)$$

More accurately, we see from Equation 2.26, that \hat{h} weighs each occupied orbital of a Slater determinant with the appropriate matrix element.

A second-quantised two-body operator is written like

$$\hat{u} = \sum_{i,j} \hat{u}(i,j) = \frac{1}{2} \sum_{ijkl} \langle ij | \hat{u} | kl \rangle \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k = \frac{1}{4} \sum_{ijkl} \langle ij | \hat{u} | kl \rangle \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k, \quad (2.28)$$

where

$$\langle ij | \hat{u} | kl \rangle \equiv \langle i(1)j(2) | \hat{u}_{12} | k(1)l(2) \rangle \quad (2.29)$$

and the antisymmetric two-electron integral for \hat{u} is abbreviated,

$$\langle ij | \hat{u} | kl \rangle - \langle ij | \hat{u} | kl \rangle = \langle ij | \hat{u} | kl \rangle \equiv \langle ij | | kl \rangle. \quad (2.30)$$

Similarly to the one-particle operator, the two-particle operator assigns the correct matrix element to pairs of single particle functions.

The second-quantised Hamiltonian can therefore be written,

$$\hat{H} = \hat{h} + \hat{u} = \sum_{ij} \hat{h}_{ij} \hat{a}_i^\dagger \hat{a}_j + \frac{1}{4} \langle ij | kl \rangle \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k. \quad (2.31)$$

2.4 Normal Order and Wick's Theorem

Bibliography

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