Quantum Mechanics I

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version September 4, 2001

Lectures given in the fall of 2001

Voorwoord

Het college Quantummechanica I wordt dit najaar verzorgd door Prof. Daan Lenstra met assistentie van Drs. Miranda van Iersel bij het werkcollege.

Het college beslaat de hoofdstukken 1 t/m 5 en 12 van het boek *Quantum Mechanics* van F. Mandl (Cambridge University Press). De aantekeningen geven soms een iets andere kijk op de stof, maar bevatten geen stof die niet ook in het boek te vinden is.

Daan Lenstra
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September 2001

Literature

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Contents

1 Observables and states

sections 1.1 and 1.2 of Mandl

The description of a physical system involves observables. In classical mechanics we are used to coordinates $\boldsymbol{r}$ and velocities $\boldsymbol{v} = \dot{\boldsymbol{r}}$ or momenta $\boldsymbol{p} = m\boldsymbol{v}$. All of these quantities are (real) numbers, attributed to the system, e.g. an electron. There are several other possible properties, like the energy of the system, in the case that the electron is moving freely given by $E = \boldsymbol{p}^2/2m$ or its angular momentum $\boldsymbol{\ell} = \boldsymbol{r} \times \boldsymbol{p}$ with respect to some origin, e.g. the atomic nucleus for an electron in an atom.

In particular for the above case of the atom one knows that the classical description in which the observables are tied to the electron as a series of numbers it is carrying around is not working. In a quantum mechanical description the observables are not tied to the system, but they refer to an appropriate measuring device. Mathematically they are described by *operators*. The physical system is then described by a *wave function*.

1.1 States ↔ wave functions

In quantum mechanics the state of a system is specified by the wave function. For a simple particle, it can be represented by a complex function depending on the position and the time,

$$\psi(\boldsymbol{r},t) \in C,$$

and it contains *all* information on such a particle. This is one of the basic assumptions of quantum mechanics. For instance

$$P(\boldsymbol{r},t)\, d^3\boldsymbol{r} = \psi^*(\boldsymbol{r},t)\psi(\boldsymbol{r},t)\, d^3\boldsymbol{r} = |\psi(\boldsymbol{r},t)|^2\, d^3\boldsymbol{r}, \tag{1}$$

gives the probability to find the particle in a volume element $d^3\boldsymbol{r}$ around the point $\boldsymbol{r}$. This definition implies that the wave functions are normalized,

$$\int d^3\boldsymbol{r}\ |\psi(\boldsymbol{r},t)|^2 = 1. \tag{2}$$

The wave functions are said to belong to a space of wave functions, a *Hilbert space* $\mathcal{H}$. The above Hilbert space is that of square integrable functions, denoted $\mathcal{H} = L^2(R^3)$.

The normalization condition can be slightly relaxed. For example, for plane waves

$$\psi(\boldsymbol{r},t) = \exp\left(i\,\boldsymbol{k}\cdot\boldsymbol{r} - i\,\omega t\right),$$

the normalization integral diverges, but the probability $|\psi|^2$ *is still finite. We will come back to this later.*

In the Hilbert space of wave functions one can add states, i.e. if $\psi_1 \in \mathcal{H}$ and $\psi_2 \in \mathcal{H}$ then also

$$\psi = c_1\,\psi_1 + c_2\,\psi_2 \tag{3}$$

is a possible state of the system, $\psi \in \mathcal{H}$. But note that

$$\begin{aligned}
|\psi|^2 &= |c_1\,\psi_1 + c_2\,\psi_2|^2 = (c_1^*\,\psi_1^* + c_2^*\,\psi_2^*)(c_1\,\psi_1 + c_2\,\psi_2) \\
&= |c_1|^2\,|\psi_1|^2 + |c_2|^2\,|\psi_2|^2 + 2\,\mathcal{R}e\,[c_1^* c_2\,\psi_1^*\psi_2] \\
&\neq |c_1|^2\,|\psi_1|^2 + |c_2|^2\,|\psi_2|^2,
\end{aligned}$$

thus probabilities are not additive! This feature is characteristic for quantum mechanics. Probabilities play the same role as intensities of light waves which are proportional to the amplitude squared. The consequence of this is that the probability shows the phenomenon of interference, illustrated in the scattering of electrons in a two-slit experiment. As lightwaves do, the probability of electrons hitting the screen shows an interference pattern.

> *Note that multiplying a normalized wave function with an overall phase factor (a complex number with length 1) has no consequences.*

Note that the normalization is a special case of a scalar product defined in the Hilbert space. We define

$$\langle \psi_1 || \psi_2 \rangle \equiv \int d^3\boldsymbol{r}\ \psi_1^*(\boldsymbol{r},t)\, \psi_2(\boldsymbol{r},t), \tag{4}$$

satisfying $\langle \psi_1 || \psi_2 \rangle = \langle \psi_2 || \psi_1 \rangle^*$.

1.2 Observables ↔ operators

What about the observables. As mentioned before they correspond with operators. If $\hat{A}$ is such an operator[1] and ψ gives a state of the system, then also $\hat{A}\psi$ is a possible state:

$$\begin{aligned} \hat{A}\ &:\ \mathcal{H} \longrightarrow \mathcal{H} \\ &\quad\ \psi \longrightarrow \hat{A}\psi \end{aligned}$$

Examples of operators are the position operator $\hat{\boldsymbol{r}}$ and the momentum operator $\hat{\boldsymbol{p}}$:

$$\hat{\boldsymbol{r}}\psi(\boldsymbol{r},t) \equiv \boldsymbol{r}\psi(\boldsymbol{r},t), \tag{5}$$

$$\hat{\boldsymbol{p}}\psi(\boldsymbol{r},t) \equiv -i\hbar\boldsymbol{\nabla}\psi(\boldsymbol{r},t). \tag{6}$$

> *Actually the operators stand for three operators, e.g. $\hat{\boldsymbol{r}} = (\hat{x},\hat{y},\hat{z})$. The quantity $\hat{x}\psi$ thus is a function in $\mathcal{H}$ of which the value in a particular point $\boldsymbol{r}$ is given by the value of the function ψ multiplied with x,*
>
> $$\hat{x}\psi(x,y,z,t) = x\,\psi(x,y,z,t).$$

The fundamental connection between the observable properties of a system and its state is given by the following postulate:

> For a system in a normed state ψ, the expectation value of the observable A, represented by the operator $\hat{A}$, is given by the quantity,
>
> $$\langle A \rangle_\psi = \langle \psi | \hat{A} | \psi \rangle = \langle \psi || \hat{A}\,\psi \rangle = \int d^3\boldsymbol{r}\ \psi^*(\boldsymbol{r},t)\, \hat{A}\psi(\boldsymbol{r},t). \tag{7}$$

Because measurements yield real numbers, suitable operators in quantum mechanics are those that lead to real expectation values. Such operators are called *hermitean* or *self-adjoint* operators.

Definition: A *hermitean* operator $\hat{A}$ is an operator for which $\langle A \rangle_\psi$ is real for all states $\psi \in \mathcal{H}$,
$\langle A \rangle_\psi = \langle A \rangle_\psi^*$ or $\int d^3\boldsymbol{r}\ \psi^*(\boldsymbol{r},t)\,\hat{A}\psi(\boldsymbol{r},t) = \int d^3\boldsymbol{r}\ (\hat{A}\psi)^*(\boldsymbol{r},t)\,\psi(\boldsymbol{r},t)$.

The expectation value is in fact a special example of what are called the *matrix elements* of $\hat{A}$,

$$\langle \psi_1 | \hat{A} | \psi_2 \rangle \equiv \int d^3\boldsymbol{r}\ \psi_1^*(\boldsymbol{r},t)\, \hat{A}\psi_2(\boldsymbol{r},t). \tag{8}$$

The expectation value $\langle A \rangle_\psi = \langle \psi | \hat{A} | \psi \rangle$ is then referred to as a *diagonal matrix element* of $\hat{A}$ in the state ψ, while $\langle \psi_1 | \hat{A} | \psi_2 \rangle$ for different states, $\psi_1 \neq \psi_2$, is referred to as a *transition matrix element.*

The operators that we will be concerned with in quantum mechanics are linear operators, which means

$$\hat{A}(c_1\psi_1 + c_2\psi_2) = c_1\,\hat{A}\psi_1 + c_2\,\hat{A}\psi_2. \tag{9}$$

For linear operators we can derive the following property for the matrix elements of a hermitean operator:

Theorem: $\hat{A}$ is hermitean $\Longleftrightarrow \langle \psi_1 | \hat{A} | \psi_2 \rangle = \langle \psi_2 | \hat{A} | \psi_1 \rangle^*$
or
$\hat{A}$ is hermitean $\Longleftrightarrow \int d^3\boldsymbol{r}\ \psi_1^*(\boldsymbol{r},t)\,\hat{A}\psi_2(\boldsymbol{r},t) = \int d^3\boldsymbol{r}\ (\hat{A}\psi_1)^*(\boldsymbol{r},t)\,\psi_2(\boldsymbol{r},t)$

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[1] The hat characterizing operators is usually omitted, but we will keep it in the first few sections

Proof: Consider the definition for the state $\psi = c_1\psi_1 + c_2\psi_2$*, where* c_1 *and* c_2 *are arbitrary. Then we have*

$$\sum_{m,n=1}^{2} c_m^* c_n \left[\langle\psi_m|\hat{A}|\psi_n\rangle - \langle\psi_n|\hat{A}|\psi_m\rangle^*\right] = 0.$$

Since c_1 *and* c_2 *are arbitrary complex numbers each term in the sum must be zero.*

In order to decide if the result of measurements of an observable is unique we consider the *standard deviation* $(\Delta A)_\psi$.

Definition: $(\Delta A)^2_\psi \equiv \langle\psi|(\hat{A} - \langle\hat{A}\rangle)^2|\psi\rangle = \int d^3\boldsymbol{r}\ \psi^*(\boldsymbol{r},t)\,(\hat{A} - \langle\hat{A}\rangle)^2\psi(\boldsymbol{r},t)$.

When in a given state ψ the observable A has a unique value the standard deviation must be zero. For a hermitean operator - for which $\langle\hat{A}\rangle_\psi$ is real - one can rewrite

$$\begin{aligned}(\Delta A)^2_\psi &= \int d^3\boldsymbol{r}\ \psi^*\,(\hat{A} - \langle\hat{A}\rangle)^2\psi \\ &= \int d^3\boldsymbol{r}\ [(\hat{A} - \langle\hat{A}\rangle)\psi]^*\,(\hat{A} - \langle\hat{A}\rangle)\psi \\ &= \int d^3\boldsymbol{r}\ |(\hat{A} - \langle\hat{A}\rangle)\psi|^2, \qquad (10)\end{aligned}$$

From this result one can immediately proof the following theorem

Theorem: $(\Delta A)_\psi = 0 \Longleftrightarrow \hat{A}\psi = a\psi$
for some number a, which in that case is precisely the expectation value of $\langle A\rangle_\psi$.

The equation $\hat{A}\psi = a\psi$ is an eigenvalue equation for the operator $\hat{A}$. Functions with this property are called *eigenfunctions* or *eigenstates* of the operator $\hat{A}$. The numbers a are called the *eigenvalues* of $\hat{A}$. The collection of eigenvalues is called the *spectrum* of $\hat{A}$.

2 Eigenvalues and eigenstates of hermitean operators

section 1.2 of Mandl

For hermitean operators we will proof some theorems for the eigenvalues and eigenstates.

Theorem: Given $\hat{A}\psi = a\psi$ and $\hat{A}$ hermitean $\Longrightarrow$ a is real.

The proof of this is trivial. Next one considers eigenfunctions.

Theorem: The eigenfunctions of a hermitean operator are orthogonal, by which we mean $\langle\psi_1||\psi_2\rangle = \int d^3\boldsymbol{r}\ \psi_1^*(\boldsymbol{r},t)\,\psi_2(\boldsymbol{r},t) = 0$.

> *Proof: First consider two different (nondegenerate) eigenvalues, i.e.* $\hat{A}\psi_1 = a_1\psi_1$ *and* $\hat{A}\psi_2 = a_2\psi_2$ *with* $a_1 \neq a_2$*. In that case both* a_1 *and* a_2 *are real and one has*
>
> $$\int d^3\boldsymbol{r}\ \psi_1^*\,\hat{A}\psi_2 = a_2 \int d^3\boldsymbol{r}\ \psi_1^*\,\psi_2,$$
>
> $$\int d^3\boldsymbol{r}\ (\hat{A}\psi_1)^*\,\psi_2 = a_1^* \int d^3\boldsymbol{r}\ \psi_1^*\,\psi_2 = a_1 \int d^3\boldsymbol{r}\ \psi_1^*\,\psi_2.$$
>
> *Hermiticity tells us that both starting expressions are equal, thus* $(a_1 - a_2)\int d^3\boldsymbol{r}\ \psi_1^*\,\psi_2 = 0$ *and thus* $\int d^3\boldsymbol{r}\ \psi_1^*\,\psi_2 = 0$.

A special case need to be considered namely the case of degenerate eigenvalues. We note that if ϕ_1 and ϕ_2 are eigenstates with the same eigenvalue a, then any linear combination $c_1\phi_1 + c_2\phi_2$ also has eigenvalue a. Thus one can defines

Definition: An eigenvalue is called s-fold degenerate if there exist s linearly independent, eigenfunctions, $\phi_1, \ldots, \phi_s$, with that particular eigenvalue.

The above proof for the orthogonality does not work for degenerate eigenvalues. But a set of s linearly independent eigenstates can be made orthogonal, e.g. via a Gramm-Schmidt procedure. Normalizing a set of orthogonal eigenstates, leads to the following conclusion[2]

Theorem: The eigenfunctions of a hermitean operator can be choosen as an *orthonormal* set, $\langle\psi_m||\psi_n\rangle = \int d^3\boldsymbol{r}\ \psi_m^*\,\psi_n = \delta_{mn}$.

The eigenfunctions, moreover, form a *complete* set of functions, which means that any state ψ can be expanded in eigenstates,

$$\psi = \sum_n c_n\,\psi_n, \tag{11}$$

where it is trivial to use the orthonormality of the basis to proof that

$$c_n = \langle\psi_n||\psi\rangle = \int d^3\boldsymbol{r}\ \psi_n^*\,\psi. \tag{12}$$

For a normed state the normalization condition $\langle\psi||\psi\rangle = \int d^3\boldsymbol{r}\ \psi^*\,\psi = 1$ implies that

$$\sum_n |c_n|^2 = 1. \tag{13}$$

Using the expansion theorem it is straightforward to write

$$\langle A\rangle_\psi = \langle\psi|\hat{A}|\psi\rangle = \sum_n |c_n|^2\,\langle A\rangle_{\psi_n} = \sum_n |c_n|^2\,a_n, \tag{14}$$

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[2]

$$\delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases}$$

where a_n are the eigenvalues corresponding to the eigenfunctions in the orthonormal set. We have assumed this to be a discrete set, but we will encounter other examples, where the summation will be changed into an integration.

For a system in a state ψ, we have the following postulate about the measurement of the observable A:

- The state ψ can be written as a superposition of eigenstates of the operator $\hat{A}$, with coefficients c_n.
- The probability to find the state ψ in an eigenstate is given by

$$P(a_n) = |c_n|^2 = |\langle\psi_n||\psi\rangle|^2, \tag{15}$$

  or more precisely (if there are degenerate eigenvalues),

$$P(a_n) = \sum_{r=1}^{s} |c_{nr}|^2, \tag{16}$$

  if c_{nr} with $r = 1, \ldots, s$ are the coefficients of s eigenstates with the same eigenvalue a_n.

- With the above probability the outcome of a measurement is a_n. Thus only the eigenvalues of $\hat{A}$ are observed! The expression for the expectation value (Eq. 14), can be rewritten

$$\langle A\rangle_\psi = \sum_n |c_n|^2\, a_n, = \sum_n P(a_n)\, a_n, \tag{17}$$

  and is consistent with the earlier postulate (Eq. 7).

- After the measurement the system is in the eigenstate ψ_n (or in a linear combination of eigenstates ψ_{nr} in case of degeneracy of a_n).

Note that the probability to find the system is in fact a special case with the operator being the unit operator $\hat{I}$.

3 The Hamiltonian

sections 1.3 and 1.4 of Mandl

The most important operator in quantum mechanics is the Hamiltonian or energy operator $\hat{H}$. It is the operator that determines the time evolution of the system,

$$i\hbar\frac{\partial\psi}{\partial t} \equiv \hat{H}\psi(\boldsymbol{r},t). \tag{18}$$

This is referred to as the Schrödinger equation. The normalization condition on wave functions (conservation of probability) requires $\hat{H}$ to be a hermitean operator.

Proof: Since the normalization states $\langle\psi||\psi\rangle = 1$, we have

$$\frac{\partial}{\partial t}\int d^3\boldsymbol{r}\ \psi^*(\boldsymbol{r},t)\psi(\boldsymbol{r},t) = 0,$$

which translates immediately into

$$\frac{1}{-i\hbar}\int d^3\boldsymbol{r}\ \left[(\hat{H}\psi)^*\psi - \psi^*(\hat{H}\psi)\right] = 0, \tag{19}$$

i.e. $\hat{H}$ is hermitean.

Next suppose that we actually know the Hamiltonian in terms of other operators, $\hat{H} = H(\hat{\boldsymbol{r}},\hat{\boldsymbol{p}},\ldots)$, e.g. for a particle with mass m in a potential $V(\boldsymbol{r})$ not depending on time,

$$\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m} + V(\hat{\boldsymbol{r}}) = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\boldsymbol{r}). \tag{20}$$

We can then look for the eigenvalues and eigenstates of this Hamiltonian,

$$\hat{H}(\hat{\boldsymbol{r}},\hat{\boldsymbol{p}},\ldots)\phi_n(\boldsymbol{r}) = E_n\phi_n(\boldsymbol{r}). \tag{21}$$

The eigenvalues are called the *energies* E_n. In that case the full time-dependent solutions of the Schrödinger equation are easily obtained. Assuming the spatial dependence to be given by $\phi_n(\boldsymbol{r})$ one finds that the time dependence is given by

$$i\hbar\frac{\partial\psi_n}{\partial t} = E_n\psi_n(\boldsymbol{r},t), \tag{22}$$

giving also the time-dependence,

$$\psi_n(\boldsymbol{r},t) = \phi_n(\boldsymbol{r})\, e^{-iE_n t/\hbar}, \tag{23}$$

which are referred to as *stationary states.* Since $\hat{H}$ is a hermitean operator it provides a complete orthonormal set of states in the Hilbert space with $\int d^3\boldsymbol{r}\ \phi_m^*\phi_n = \delta_{mn}$. which we (for simplicity) have taken to be countable.

Let us consider the case that the potential is zero. In that case the solutions of

$$-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\,\phi(\boldsymbol{r}) = E\,\phi(\boldsymbol{r}) \tag{24}$$

are the plane waves

$$\phi_k(\boldsymbol{r}) = \exp(i\boldsymbol{k}\cdot\boldsymbol{r}) \qquad \textit{with} \qquad E = \frac{\hbar^2\boldsymbol{k}^2}{2m}. \tag{25}$$

They form an infinite set of solutions characterized by the wave vector $\boldsymbol{k}$. The full time-dependent solution is

$$\psi_k(\boldsymbol{r},t) = \exp(i\boldsymbol{k}\cdot\boldsymbol{r} - i\omega\,t), \tag{26}$$

where $\omega(\boldsymbol{k}) = \hbar\boldsymbol{k}^2/2m$.

In general, a physical system is not necessarily in an eigenstate of the Hamiltonian. We consider two situations:
(1) The state of the system is one of the eigenstates of the Hamiltonian,

$$\psi_n(\boldsymbol{r},t) = \phi_n(\boldsymbol{r})\, e^{-iE_n t/\hbar}. \tag{27}$$

In that case one has the following properties.

- $$P(\boldsymbol{r})\, d^3\boldsymbol{r} = |\psi_n(\boldsymbol{r},t)|^2\, d^3\boldsymbol{r} = |\phi_n(\boldsymbol{r})|^2\, d^3\boldsymbol{r},$$

  or stated in words, the probability to find the system at a particular place is time-independent.

- If $\hat{A}$ is an operator without explicit time dependence (e.g. I, $\hat{\boldsymbol{r}}$, $\hat{\boldsymbol{p}}$) then

  $$\langle A\rangle_n(t) = \int d^3\boldsymbol{r}\ \psi_n^*(\boldsymbol{r},t)\hat{A}\psi_n(\boldsymbol{r},t) = \int d^3\boldsymbol{r}\ \phi_n^*(\boldsymbol{r})\hat{A}\phi_n(\boldsymbol{r}) = \langle A\rangle_n,$$

  which is independent of the time.

(2) The state of the system is a superposition of eigenstates of the Hamiltonian, for simplicity consider two states and use $E_n \equiv \hbar\omega_n$,

$$\psi(\boldsymbol{r},t) = c_1\,\phi_1(\boldsymbol{r})\, e^{-iE_1 t/\hbar} + c_2\,\phi_2(\boldsymbol{r})\, e^{-iE_2 t/\hbar}. \tag{28}$$

The expectation value of an operator $\hat{A}$ in this case is not time-independent. Defining the matrix elements

$$\int d^3\boldsymbol{r}\ \phi_1^*(\boldsymbol{r})\,\hat{A}\phi_1(\boldsymbol{r}) = A_{11}, \tag{29}$$

$$\int d^3\boldsymbol{r}\ \phi_2^*(\boldsymbol{r})\,\hat{A}\phi_2(\boldsymbol{r}) = A_{22}, \tag{30}$$

$$\int d^3\boldsymbol{r}\ \phi_1^*(\boldsymbol{r})\,\hat{A}\phi_2(\boldsymbol{r}) = A_{12}, \tag{31}$$

$$\int d^3\boldsymbol{r}\ \phi_2^*(\boldsymbol{r})\,\hat{A}\phi_1(\boldsymbol{r}) = A_{21} = A_{12}^*, \tag{32}$$

one obtains

$$\begin{aligned} \langle A\rangle(t) &= \int d^3\boldsymbol{r}\ \psi^*(\boldsymbol{r},t)\hat{A}\psi(\boldsymbol{r},t) \\ &= |c_1|^2\, A_{11} + |c_2|^2\, A_{22} + 2\,\mathcal{R}e\left[c_1^* c_2\, A_{12}\, e^{i(\omega_1-\omega_2)t}\right]. \end{aligned} \tag{33}$$

One sees the occurrence of oscillations with a frequency

$$\omega_{osc} = \omega_1 - \omega_2 = \frac{E_1 - E_2}{\hbar}. \tag{34}$$

4 Multi-particle systems

For more than one particle the system is described by a (complex-valued) wave function

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N, t) \in C.$$

The wave function acts in a configuration space $R^3 \otimes R^3 \otimes \ldots$. The probability to find the system is given by

$$P(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N, t)\; d^3\boldsymbol{r}_1 \ldots d^3\boldsymbol{r}_N = |\psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N, t)|^2\; d^3\boldsymbol{r}_1 \ldots d^3\boldsymbol{r}_N, \tag{35}$$

Operators acting on the wave function are e.g. $\hat{\boldsymbol{r}}_1$, $\hat{\boldsymbol{r}}_2$, ... or $\hat{\boldsymbol{p}}_1 = -i\hbar\boldsymbol{\nabla}_1$, etc. Note that $\hat{\boldsymbol{r}_1}$ only works in one (the first) of the subspaces of the full configuration space. Formally this operator should read $\hat{\boldsymbol{r}}_1 \otimes I_2 \otimes \ldots$, but you can imagine that we will not often use this notation. The hamiltonian again determines the time evolution,

$$\hat{H} = i\hbar\frac{\partial}{\partial t}, \tag{36}$$

and we are in business when we also know the hamiltonian in terms of the other operators,

$$\hat{H} = H(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{p}}_1, \hat{\boldsymbol{r}}_2, \hat{\boldsymbol{p}}_2, \ldots). \tag{37}$$

A particular easy multi-particle system is the one for which the hamiltonian is separable, e.g. if for two particles

$$H(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{p}}_1, \hat{\boldsymbol{r}}_2, \hat{\boldsymbol{p}}_2) = H_1(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{p}}_1) + H_2(\hat{\boldsymbol{r}}_2, \hat{\boldsymbol{p}}_2). \tag{38}$$

It is trivial to proof the following theorem.

Theorem: If we know the solutions for $\hat{H}_1$ and $\hat{H}_2$,

$$\hat{H}_1\, \phi_m^{(1)}(\boldsymbol{r}_1) = E_m^{(1)}\, \phi_m^{(1)}(\boldsymbol{r}_1),$$
$$\hat{H}_2\, \phi_n^{(2)}(\boldsymbol{r}_2) = E_n^{(2)}\, \phi_n^{(2)}(\boldsymbol{r}_2),$$

then we know that the eigenstates and eigenvalues, $\hat{H}\,\phi = E\,\phi$, for $\hat{H} = \hat{H}_1 + \hat{H}_2$ are given by

$$\phi_{m,n}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \phi_m^{(1)}(\boldsymbol{r}_1)\, \phi_n^{(2)}(\boldsymbol{r}_2),$$
$$E_{m,n} = E_m^{(1)} + E_n^{(2)}.$$

Of course it may sometimes be necessary to do a little bit of work to make a hamiltonian separable. For instance, the hamiltonian

$$\hat{H} = \frac{\hat{\boldsymbol{p}_1}^2}{2m_1} + \frac{\hat{\boldsymbol{p}_2}^2}{2m_2} + V(\hat{\boldsymbol{r}_1} - \hat{\boldsymbol{r}_2}) = -\frac{\hbar^2}{2m_1}\boldsymbol{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\boldsymbol{\nabla}_2^2 + V(\boldsymbol{r}_1 - \boldsymbol{r}_2), \tag{39}$$

is non-separable. However, after changing to center of mass and relative coordinates,

$$\boldsymbol{R} \equiv \frac{m_1}{M}\boldsymbol{r}_1 + \frac{m_2}{M}\boldsymbol{r}_2, \tag{40}$$

$$\boldsymbol{r} \equiv \boldsymbol{r}_1 - \boldsymbol{r}_2, \tag{41}$$

where $M = m_1 + m_2$, it is easy to proof (Exercise 1.5, Mandl) that

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2M}\boldsymbol{\nabla}_R^2}_{H_{CM}} \underbrace{-\frac{\hbar^2}{2\mu}\boldsymbol{\nabla}_r^2 + V(\boldsymbol{r})}_{H_{rel}}, \tag{42}$$

with reduced mass $\mu = m_1 m_2/M$. Thus we end up with a separable problem in terms of the hamiltonian $H_{CM}(\boldsymbol{R}, \boldsymbol{P})$ for the CM coordinates and the hamiltonian $H_{rel}(\boldsymbol{r}, \boldsymbol{p})$ for the relative coordinates, where

$$\hat{\boldsymbol{P}} \equiv -i\hbar\,\boldsymbol{\nabla}_R = -i\hbar\,(\boldsymbol{\nabla}_1 + \boldsymbol{\nabla}_2) = \hat{\boldsymbol{p}}_1 + \hat{\boldsymbol{p}}_2, \tag{43}$$

$$\hat{\boldsymbol{p}} \equiv -i\hbar\,\boldsymbol{\nabla}_r = -i\hbar\left(\frac{m_2}{M}\boldsymbol{\nabla}_1 - \frac{m_1}{M}\boldsymbol{\nabla}_2\right) = \frac{m_2}{M}\hat{\boldsymbol{p}}_1 - \frac{m_1}{M}\hat{\boldsymbol{p}}_2. \tag{44}$$

5 Probability and current

The local probability in a state described with the wave function $\psi(\boldsymbol{r},t)$ is given by

$$\rho(\boldsymbol{r},t) = |\psi(\boldsymbol{r},t)|^2. \tag{45}$$

The time-dependence indicates that locally the probability can change, implying a current $\boldsymbol{j}(\boldsymbol{r},t)$. This current should be such that it satisfies the continuity equation,

$$\frac{\partial}{\partial t}\,\rho + \boldsymbol{\nabla}\cdot\boldsymbol{j} = 0, \tag{46}$$

since this implies for a finite volume V surrounded by a surface S one has (using Stokes' law) the property

$$-\frac{d}{dt}\int_V d^3\boldsymbol{r}\;\rho(\boldsymbol{r},t) = \int_V d^3\boldsymbol{r}\;\boldsymbol{\nabla}\cdot\boldsymbol{j}(\boldsymbol{r},t) = \int_S d^2\boldsymbol{s}\cdot\boldsymbol{j}(\boldsymbol{r},t), \tag{47}$$

i.e. what leaks out of the volume V must appear as a current flowing through the surface S. Using the fact that the time-evolution of the wave function and thus the density is determined by the hamiltonian (see Eq. 19) one finds that for a commonly used hamiltonian like the one in Eq. 20 the current is given by

$$\boldsymbol{j}(\boldsymbol{r},t) = \frac{i\hbar}{2m}\left[(\boldsymbol{\nabla}\psi)^*\psi - \psi^*(\boldsymbol{\nabla}\psi)\right] \tag{48}$$

(Exercise 1.6, Mandl).

6 Other degrees of freedom

Often a system has additional degrees of freedom and we need to extend the wave function. The most well-known example is spin. It turns out that for a proper description of an electron, one needs to specify in addition to $\psi(\boldsymbol{r},t)$ a spin wave function χ, i.e. an electron is specified by

$$\psi(\boldsymbol{r},t)\,\chi(t)$$

which however can take only two values, spin-up or spin-down. Thus one can write

$$\chi_\uparrow(t_0) \equiv \left(\begin{array}{c} 1 \\ 0 \end{array}\right), \qquad \chi_\downarrow(t_0) \equiv \left(\begin{array}{c} 0 \\ 1 \end{array}\right). \tag{49}$$

Since the Hilbert space of allowed wave functions contains all linear combinations one immediately sees that after the choice of the spin-up and spin-down basis-states, the wave function can be written as

$$\left(\begin{array}{c} \psi_\uparrow(\boldsymbol{r},t) \\ \psi_\downarrow(\boldsymbol{r},t) \end{array}\right).$$

The number of allowed operators in the spin-space for an electron is actually very limited. Linear operators in the spin-space can be represented as 2×2 matrices. There exist only four linearly independent *hermitean* 2×2 matrices, namely the unit-operator and the three *Pauli matrices*

$$\sigma_x = \left(\begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array}\right), \qquad \sigma_y = \left(\begin{array}{cc} 0 & -i \\ i & 0 \end{array}\right), \qquad \sigma_z = \left(\begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array}\right). \tag{50}$$

As an example of the appearance of spin operators, we mention the hamiltonian for an electron in a magnetic field,

$$H = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \mu_B\,\boldsymbol{\sigma}\cdot\boldsymbol{B}. \tag{51}$$

where $\mu_B = e\hbar/2m$ *for an electron is the socalled Bohr magneton* ($\mu_B \approx 5.8\times 10^{-5}$ *eV/T*). *Writing*

$$\left(\begin{array}{c} \psi_\uparrow(\boldsymbol{r},t) \\ \psi_\downarrow(\boldsymbol{r},t) \end{array}\right) = \left(\begin{array}{c} \phi_\uparrow(\boldsymbol{r}) \\ \phi_\downarrow(\boldsymbol{r}) \end{array}\right) e^{-iEt/\hbar} \tag{52}$$

and solving the time-independent Schrödinger equation for ϕ, *one notices that the above hamiltonian is actually also separable, since the first term only works in* $\boldsymbol{r}$*-space, while the second part only works in the spin-space. Thus the (time-independent) wave function factorizes,*

$$\left(\begin{array}{c} \phi_\uparrow(\boldsymbol{r}) \\ \phi_\downarrow(\boldsymbol{r}) \end{array}\right) = \phi(\boldsymbol{r}) \left(\begin{array}{c} c_\uparrow \\ c_\downarrow \end{array}\right). \tag{53}$$

The $\boldsymbol{r}$*-dependent part are the plane wave solutions* $\phi_k(\boldsymbol{r}) = \exp(i\boldsymbol{k}\cdot\boldsymbol{r})$ *with* $E(\boldsymbol{k}) = \hbar^2\boldsymbol{k}^2/2m$. *The solutions of the second part, not surprisingly, are two orthogonal vectors. Suppose the* $\boldsymbol{B}$ *field is given by* $\boldsymbol{B} = (B\sin\theta,\ 0, B\cos\theta)$, *then we need the eigenvectors and eigenvalues of*

$$\hat{H}_{mag} = \mu_B B \left(\begin{array}{cc} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{array}\right), \tag{54}$$

which are

$$\chi_1 = \left(\begin{array}{c} \cos(\theta/2) \\ \sin(\theta/2) \end{array}\right), \qquad \chi_2 = \left(\begin{array}{c} -\sin(\theta/2) \\ \cos(\theta/2) \end{array}\right), \tag{55}$$

with $E_{1,mag} = +\mu_B\,B$ *and* $E_{2,mag} = -\mu_B\,B$. *For instance for a magnetic field in the z-direction the solutions are precisely the states defined in Eq. 49, while for a magnetic field in the x-direction the solutions are a particular linear combination of these states,*

$$\chi_1 = \frac{1}{\sqrt{2}}\left(\begin{array}{c} 1 \\ 1 \end{array}\right) = (\chi_\uparrow + \chi_\downarrow)/\sqrt{2}, \qquad \chi_2 = \frac{1}{\sqrt{2}}\left(\begin{array}{c} -1 \\ 1 \end{array}\right) = (\chi_\downarrow - \chi_\uparrow)/\sqrt{2}. \tag{56}$$

7 Dirac notation

7.1 Space of states = ket-space (Hilbert space)

- Quantum mechanical states are denoted $|u\rangle$ and form a linear vector space over the complex numbers (C), the Hilbert space $\mathcal{H} = \{|u\rangle\}$,

$$\left.\begin{array}{l} |u_1\rangle \in \mathcal{H} \\ |u_2\rangle \in \mathcal{H} \\ c_1, c_2 \in C \end{array}\right\} \longrightarrow c_1|u_1\rangle + c_2|u_2\rangle \in \mathcal{H} \tag{57}$$

- Given a basis $\{|u_1\rangle, \ldots, |u_1\rangle\}$ for an N-dimensional Hilbert-space (N can be infinite!) consisting of a collection linearly independent kets, we can express every ket in this basis (*completeness*),

$$|u\rangle \in \mathcal{H} \longrightarrow |u\rangle = \sum_{n=1}^{N} c_n|u_n\rangle. \tag{58}$$

7.2 Scalar product and the (dual) bra-space

For elements $|u\rangle$, $|v\rangle \in \mathcal{H}$ we can construct the complex number $\langle u||v\rangle \in C$, for which

- $\langle u||v\rangle^* = \langle v||u\rangle$,
- If $|u\rangle = c_1|u_1\rangle + c_2|u_2\rangle$ then $\langle v||u\rangle = c_1\langle v||u_1\rangle + c_2\langle v||u_2\rangle$.
  Note that this implies

$$\begin{aligned} \langle u||v\rangle &= \langle v||u\rangle^* = c_1^*\langle v||u_1\rangle^* + c_2^*\langle v||u_2\rangle^* \\ &= c_1^*\langle u_1||v\rangle + c_2^*\langle u_2||v\rangle. \end{aligned}$$

- $\langle u||u\rangle \geq 0$.

Beside the ket-space we can also introduce the dual bra-space, $\mathcal{H}^* = \{\langle u|\}$, which is anti-linear meaning that

$$|u\rangle = c_1|u_1\rangle + c_2|u_2\rangle \longleftrightarrow \langle u| = c_1^*\langle u_1| + c_2^*\langle u_2|. \tag{59}$$

The scalar product is constructed from a bra-vector and a ket-vector ("bra(c)ket").

7.3 Orthonormal basis

A state $|u\rangle$ is *normalized* when $\langle u||u\rangle = 1$. Two states $|u\rangle$ and $|v\rangle$ are orthogonal when $\langle u||v\rangle = 0$. In a linear vector space an orthonormal basis can be constructed, in which every state can be expanded,

- Basis $\{|u_1\rangle, |u_2\rangle, \ldots\}$ with $\langle u_m||u_n\rangle = \delta_{mn}$.
- If $|u\rangle = \sum_n c_n|u_n\rangle$, then $c_n = \langle u_n||u\rangle$ (proof) and we can write

$$|u\rangle = \sum_n |u_n\rangle \underbrace{\langle u_n||u\rangle}_{c_n} = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}. \tag{60}$$

- Note that

$$\langle u||u\rangle = 1 \longleftrightarrow \sum_n |c_n|^2 = 1, \tag{61}$$

  hence the name *probability amplitude* for c_n.
- The collection $\{\langle u_1|, \langle u_2|, \ldots\}$ forms an orthonormal basis for the bra-space.

7.4 Operators

- An operator A acts in the Hilbert-space $\mathcal{H}$, i.e. $|v\rangle = A|u\rangle = |Au\rangle \in \mathcal{H}$.
- If $|u\rangle = c_1|u_1\rangle + c_2|u_2\rangle$ then $A|u\rangle = c_1\, A|u_1\rangle + c_2\, A|u_2\rangle$ (A is linear).
- The matrix element of A in states $|u\rangle$ and $|v\rangle$ is given by

  $$\langle u|A|v\rangle.$$

  If $|u\rangle = |v\rangle$ we call this *expectation value* of A, if $|u\rangle \neq |v\rangle$ we call this *transition matrix element.*
- The unit operator acts as $I|u\rangle = |u\rangle$ and can with the help of a complete orthornormal basis $\{|u_n\rangle\}$ be written as

  $$I = \sum_n |u_n\rangle\langle u_n|, \tag{62}$$

  directly following from Eq. 60 and known as *completeness relation.*
- If $|u\rangle = \sum_n c_n|u_n\rangle = \sum_n |u_n\rangle\langle u_n||u\rangle$ then we can write for $A|u\rangle$

  $$\begin{aligned} A|u\rangle &= \sum_n A|u_n\rangle\langle u_n||u\rangle \\ &= \sum_{m,n} |u_m\rangle \underbrace{\langle u_m|A|u_n\rangle}_{A_{mn}} \underbrace{\langle u_n||u\rangle}_{c_n} = \sum_m |u_m\rangle \left(\sum_n A_{mn}c_n\right) \\ &= \begin{pmatrix} A_{11} & A_{12} & \dots \\ A_{21} & A_{22} & \dots \\ \vdots & \vdots & \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} \end{aligned} \tag{63}$$

  and the matrix element of A is given by

  $$\begin{aligned} \langle u|A|u\rangle &= \sum_{m,n} \underbrace{\langle u||u_m\rangle}_{c_m^*} \underbrace{\langle u_m|A|u_n\rangle}_{A_{mn}} \underbrace{\langle u_n||u\rangle}_{c_n} \\ &= (c_1^*\ c_2^*\ \dots) \begin{pmatrix} A_{11} & A_{12} & \dots \\ A_{21} & A_{22} & \dots \\ \vdots & \vdots & \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} \end{aligned} \tag{64}$$

7.5 Adjoint operator

Given an operator A, the adjoint operator $A^\dagger$ is defined by giving its matrix elements in terms of those of A,

$$\langle u|A^\dagger|v\rangle \equiv \langle v|A|u\rangle^*. \tag{65}$$

We note that de bra-state $\langle Au| = \langle u|A^\dagger$. This is proven in the following way: for every $|v\rangle$ is $\langle Au||v\rangle = \langle v||Au\rangle^* = \langle v|A|u\rangle^* = \langle u|A^\dagger|v\rangle$.

7.6 Hermitean operators

- Definition: An operator A is hermitean when $\langle u||Au\rangle = \langle Au||u\rangle$.
  By applying this on a state $c_1|u\rangle + c_2|v\rangle$ with arbitrary coefficients one sees that this is equivalent with

  $$\langle u||Av\rangle = \langle Au||v\rangle \leftrightarrow \langle u|A|v\rangle = \langle u|A^\dagger|v\rangle \leftrightarrow A = A^\dagger,$$

  i.e. A is self-adjoint.

- The consequences of $A = A^\dagger$ for transition matrix elements and expectation values are

$$\langle u|A|v\rangle = \langle u|A^\dagger|v\rangle = \langle v|A|u\rangle^* \tag{66}$$

$$\langle u|A|u\rangle = \langle u|A|u\rangle^* \quad \rightarrow \quad \text{real expectation values} \tag{67}$$

- For the eigenvalues (a_n) and eigenstates ($|n\rangle$),

$$A|n\rangle = a_n|n\rangle \tag{68}$$

  of a hermitean operator we have

  - Choose $\langle n||n\rangle = 1$.
  - $\langle n|A|n\rangle = a_n$ are the (real) eigenvalues.
  - Eigenstates corresponding with nondegenerate eigenvalues are orthogonal,

$$\left.\begin{array}{l} A|n\rangle = a_n|n\rangle \\ A|m\rangle = a_m|m\rangle \\ a_m \neq a_n \end{array}\right\} \longrightarrow \langle m||n\rangle = 0.$$

    If eigenvalues are degenerate, we can construct orthogonal eigenstates (possibly by using other, commuting, operators).
  - Thus, eigenstates form an orthonormal basis, $\langle m||n\rangle = \delta_{mn}$. Using this basis A is diagonal,

$$A = \sum_n |n\rangle a_n \langle n| = \begin{pmatrix} a_1 & 0 & \dots \\ 0 & a_2 & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \tag{69}$$

- The expectation value of a hermitean operator can be written as

$$\langle u|A|u\rangle = \sum_n \underbrace{\langle u||n\rangle}_{c_n^*} a_n \underbrace{\langle n||u\rangle}_{c_n} = \sum_n a_n\,|c_n|^2. \tag{70}$$

  This coincides with the interpretation of $|c_n|^2$ as the probability to find the state $|n\rangle$ and obtain the result a_n in a measurement.

7.7 Unitary operators

- Definition: An operator U is unitary when $U^{-1} = U^\dagger$, or $UU^\dagger = U^\dagger U = I$.
- It is trivial to prove that a unitary operator conserves scalar products,

$$\langle Uv||Uw\rangle = \langle v||w\rangle \tag{71}$$

  With the help of a unitary matrix we can transform an orthonormal basis $\{|u_n\rangle\}$ in another such basis $\{U|u_n\rangle\}$.

7.8 Coordinate-representation

- Considering the hermitean operator $\hat{\boldsymbol{r}}$ we denote the eigenstates as $|\boldsymbol{r}\rangle$ and the eigenvalues as $\boldsymbol{r}$. Thus

$$\hat{\boldsymbol{r}}|\boldsymbol{r}\rangle = \boldsymbol{r}|\boldsymbol{r}\rangle, \tag{72}$$

  with the following properties;

  - (i) Orthogonality[3]: $\langle \boldsymbol{r}||\boldsymbol{r}'\rangle = \delta^3(\boldsymbol{r} - \boldsymbol{r}')$

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[3] Definition of δ-function: $\int_{-\infty}^{\infty} dz\, f(z)\delta(z-a) \equiv f(a)$

  - (ii) Expansion of state: $|\psi\rangle = \int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle\, \underbrace{\langle \boldsymbol{r}||\psi\rangle}_{\psi(\boldsymbol{r})}$
  - (iii) Identity: $I = \int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle\langle\boldsymbol{r}|$
  - (iv) Operator expansion: $\hat{\boldsymbol{r}} = \int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle\boldsymbol{r}\langle\boldsymbol{r}|$

- We check that the above is consistent and agrees with the wave formulation of quantum mechanics:
  - Consistency of (ii) with (i) and (iii):
    $\langle\boldsymbol{r}'||\psi\rangle = \int d^3\boldsymbol{r}\ \langle\boldsymbol{r}'||\boldsymbol{r}\rangle\langle\boldsymbol{r}||\psi\rangle = \int d^3\boldsymbol{r}\ \delta^3(\boldsymbol{r}-\boldsymbol{r}')\,\psi(\boldsymbol{r}) = \psi(\boldsymbol{r}')$
  - From the definition we have $\hat{\boldsymbol{r}}\psi(\boldsymbol{r}) = \langle\boldsymbol{r}|\hat{\boldsymbol{r}}|\psi\rangle = \boldsymbol{r}\,\langle\boldsymbol{r}||\psi\rangle = \boldsymbol{r}\,\psi(\boldsymbol{r})$
  - Normalization of $\psi(\boldsymbol{r})$: $\langle\psi||\psi\rangle = \int d^3\boldsymbol{r}\ \underbrace{\langle\psi||\boldsymbol{r}\rangle}_{\psi^*(\boldsymbol{r})}\underbrace{\langle\boldsymbol{r}||\psi\rangle}_{\psi(\boldsymbol{r})} = \int d^3\boldsymbol{r}\ |\psi(\boldsymbol{r})|^2 = 1$
  - Scalar product: $\langle\psi||\phi\rangle = \int d^3\boldsymbol{r}\ \underbrace{\langle\psi||\boldsymbol{r}\rangle}_{\psi^*(\boldsymbol{r})}\underbrace{\langle\boldsymbol{r}||\phi\rangle}_{\phi(\boldsymbol{r})} = \int d^3\boldsymbol{r}\ \psi^*(\boldsymbol{r})\phi(\boldsymbol{r})$
  - Expectation value: $\langle\psi|\hat{\boldsymbol{r}}|\psi\rangle = \int d^3\boldsymbol{r}\ \langle\psi||\boldsymbol{r}\rangle\boldsymbol{r}\langle\boldsymbol{r}||\psi\rangle = \int d^3\boldsymbol{r}\ \boldsymbol{r}\,|\psi(\boldsymbol{r})|^2$

- Other operators are among others

$$f(\hat{\boldsymbol{r}}) = \int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle f(\boldsymbol{r})\langle\boldsymbol{r}|, \tag{73}$$

$$\hat{\boldsymbol{p}} = \int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle\,(-i\hbar\boldsymbol{\nabla})\,\langle\boldsymbol{r}|. \tag{74}$$

It is simple to check that $[r_i, p_j] = i\hbar\delta_{ij}$ and that $\hat{\boldsymbol{p}}\psi(\boldsymbol{r}) = -i\hbar\,\boldsymbol{\nabla}\psi(\boldsymbol{r})$.

7.9 Momentum-representation

- Consider the hermitean operator $\hat{\boldsymbol{p}}$ and denote the eigenstates as $|\boldsymbol{p}\rangle$ and the eigenvalues as $\boldsymbol{p}$. Thus

$$\hat{\boldsymbol{p}}|\boldsymbol{p}\rangle = \boldsymbol{p}|\boldsymbol{p}\rangle. \tag{75}$$

- We already saw the coordinate representation, consistent with the commutation relation $[r_i, p_j] = i\hbar\delta_{ij}$ and thus we can determine $\langle\boldsymbol{r}||\boldsymbol{p}\rangle$:

$$\hat{\boldsymbol{p}}\psi_p(\boldsymbol{r}) = \boldsymbol{p}\psi_p(\boldsymbol{r}) \ \longrightarrow\ \underbrace{\psi_p(\boldsymbol{r})}_{\langle\boldsymbol{r}||\boldsymbol{p}\rangle} = \sqrt{\rho}\,\exp\left(\frac{i}{\hbar}\,\boldsymbol{p}\cdot\boldsymbol{r}\right) \tag{76}$$

(This defines ρ).

- We have the following properties:
  - (i) Orthogonality: $\langle\boldsymbol{p}||\boldsymbol{p}'\rangle = \rho\,(2\pi\hbar)^3\,\delta^3(\boldsymbol{p}-\boldsymbol{p}')$
  - (ii) Expansion of state: $|\psi\rangle = \int \frac{d^3p}{(2\pi\hbar)^3\,\rho}\ |\boldsymbol{p}\rangle\,\underbrace{\langle\boldsymbol{p}||\psi\rangle}_{\tilde{\psi}(\boldsymbol{p})}$
  - (iii) Identity: $I = \int \frac{d^3p}{(2\pi\hbar)^3\,\rho}\ |\boldsymbol{p}\rangle\langle\boldsymbol{p}|$
  - (iv) Operator expansion: $\hat{\boldsymbol{p}} = \int \frac{d^3p}{(2\pi\hbar)^3\,\rho}\ |\boldsymbol{p}\rangle\boldsymbol{p}\langle\boldsymbol{p}|$

- Switching of representation,

$$\begin{aligned}
\psi(\boldsymbol{r}) = \langle \boldsymbol{r} || \psi\rangle &= \int \frac{d^3\boldsymbol{p}}{(2\pi\hbar)^3\,\rho}\,\langle \boldsymbol{r}||\boldsymbol{p}\rangle\langle\boldsymbol{p}||\psi\rangle \\
&= \int \frac{d^3\boldsymbol{p}}{(2\pi\hbar)^3\,\sqrt{\rho}}\,\exp\left(\frac{i}{\hbar}\,\boldsymbol{p}\cdot\boldsymbol{r}\right)\tilde{\psi}(\boldsymbol{p}), \qquad (77) \\
\tilde{\psi}(\boldsymbol{p}) = \langle \boldsymbol{p} || \psi\rangle &= \int d^3\boldsymbol{r}\,\langle\boldsymbol{p}||\boldsymbol{r}\rangle\langle\boldsymbol{r}||\psi\rangle \\
&= \int d^3\boldsymbol{r}\,\sqrt{\rho}\,\exp\left(-\frac{i}{\hbar}\,\boldsymbol{p}\cdot\boldsymbol{r}\right)\psi(\boldsymbol{r}), \qquad (78)
\end{aligned}$$

  means Fourier transforming. Choices for the normalization of plane waves are $\rho = 1$ or $\rho = (2\pi\hbar)^{-3}$ (non-relativistic) or $\rho = 2E$ (relativistic).

- Consistency of Eq. 76 and (iv):

$$\begin{aligned}
\langle\boldsymbol{r}|\hat{\boldsymbol{p}}|\psi\rangle &= \int \frac{d^3\boldsymbol{p}}{(2\pi\hbar)^3\,\rho}\,\langle\boldsymbol{r}||\boldsymbol{p}\rangle\boldsymbol{p}\langle\boldsymbol{p}||\psi\rangle = \int \frac{d^3\boldsymbol{p}}{(2\pi\hbar)^3\sqrt{\rho}}\,\boldsymbol{p}\,\exp\left(\frac{i}{\hbar}\,\boldsymbol{p}\cdot\boldsymbol{r}\right)\tilde{\psi}(\boldsymbol{p}) \\
&= -i\hbar\boldsymbol{\nabla}\int\frac{d^3\boldsymbol{p}}{(2\pi\hbar)^3\sqrt{\rho}}\,\exp\left(\frac{i}{\hbar}\,\boldsymbol{p}\cdot\boldsymbol{r}\right)\tilde{\psi}(\boldsymbol{p}) = -i\hbar\boldsymbol{\nabla}\psi(\boldsymbol{r}) \qquad (79)
\end{aligned}$$

8 Inversion and Inversion Symmetry

section 4.1 (Mandl)

For coordinates, inversion means:

$$\boldsymbol{r} \longrightarrow -\boldsymbol{r} \qquad \text{and} \qquad t \longrightarrow t, \tag{80}$$

implying for instance that classically for $\boldsymbol{p} = m\dot{\boldsymbol{r}}$ and $\boldsymbol{\ell} = \boldsymbol{r} \times \boldsymbol{p}$ one has

$$\boldsymbol{p} \longrightarrow -\boldsymbol{p} \qquad \text{and} \qquad \boldsymbol{\ell} \longrightarrow \boldsymbol{\ell}. \tag{81}$$

The same is true for the quantummechanical operators, e.g. $\boldsymbol{p} = -i\hbar\,\boldsymbol{\nabla}$.

We study the properties of a system under inversion, specifically in the situation that inversion leaves the system invariant. In quantum mechanics the latter is the case when the hamiltonian is invariant, which means

$$H(\boldsymbol{r}, \boldsymbol{p}, \ldots) = H(-\boldsymbol{r}, -\boldsymbol{p}, \ldots). \tag{82}$$

(i) A first examples of such a hamiltonian is that for one particle in a central potential,

$$H = \frac{\boldsymbol{p}^2}{2m} + V(r).$$

(ii) As another example, consider an electron in a diatomic molecule with a potential

$$V(\boldsymbol{r}) = V_1(|\boldsymbol{r} + \boldsymbol{a}|) + V_2(|\boldsymbol{r} - \boldsymbol{a}|),$$

where V_1 and V_2 are the Coulomb potentials for charges $Z_1\,e$ and $Z_2\,e$ respectively. One has inversion invariance only for the case that $V_1 = V_2$.

Consider an eigenstate of the hamiltonian,

$$H(\boldsymbol{r}, \boldsymbol{p})\phi(\boldsymbol{r}) = E\phi(\boldsymbol{r}) \tag{83}$$

This is an expression valid for all $\boldsymbol{r}$, thus also

$$H(-\boldsymbol{r}, -\boldsymbol{p})\phi(-\boldsymbol{r}) = E\phi(-\boldsymbol{r}) \tag{84}$$

(note $\boldsymbol{p} = -i\hbar\boldsymbol{\nabla}$). Invariance of the hamiltonian implies

$$H(\boldsymbol{r}, \boldsymbol{p})\phi(-\boldsymbol{r}) = E\phi(-\boldsymbol{r}). \tag{85}$$

This means that for an inversion-invariant hamiltonian one has two solutions $\phi_1(\boldsymbol{r}) = \phi(\boldsymbol{r})$ and $\phi_2(\boldsymbol{r}) = \phi(-\boldsymbol{r})$ with the same energy.
(i) If E is *non-degenerate* one has $\phi_1(\boldsymbol{r}) = c\,\phi_2(\boldsymbol{r})$, i.e. $\phi(\boldsymbol{r}) = c\,\phi(-\boldsymbol{r})$. This again is valid for all $\boldsymbol{r}$ and thus $\phi(-\boldsymbol{r}) = c\,\phi(\boldsymbol{r})$ giving $c^2 = 1$ and $c = 1$ or $c = -1$. Thus ϕ is *even* or ϕ is *odd.*
(ii) If E is degenerate, $\phi_1(\boldsymbol{r}) = \phi(\boldsymbol{r})$ and $\phi_2 = \phi(-\boldsymbol{r})$ need not be dependent, but in that case any linear combinations $a\,\phi_1 + b\,\phi_2$ has also energy E, in particular

$$\phi_\pm(\boldsymbol{r}) = \phi(\boldsymbol{r}) \pm \phi(-\boldsymbol{r}) \tag{86}$$

are *even* and *odd* eigenfunctions, respectively.
Conclusion: If the hamiltonian H is invariant under inversion, its eigenfuncties are *even* or *odd.*

9 Inversion and the Parity operator

section 4.1 (Mandl)

In quantum mechanics the states $|\psi\rangle$ are characterized by functions $\psi(\boldsymbol{r},t)$. In the configuration space we know the result of inversion, $\boldsymbol{r} \to -\boldsymbol{r}$ and $t \to t$, in the case of more particles generalized to $\boldsymbol{r}_i \to -\boldsymbol{r}_i$ and $t \to t$. What is happening in the Hilbert space of wave functions. We can just define the action on functions, $\psi \to \psi' \equiv P\psi$ in such a way that $\psi'(\boldsymbol{r}') = \psi(\boldsymbol{r})$. This means for inversion

$$P\phi(-\boldsymbol{r}) \equiv \phi(\boldsymbol{r}) \quad \Longrightarrow \quad P\phi(\boldsymbol{r}) = \phi(-\boldsymbol{r}). \tag{87}$$

The function $P\phi$ is the new wave function obtained by the action of the *parity operator* P. It is a hermitian operator.

P is hermitean since $\int d^3r\ \phi^*(\boldsymbol{r})\,P\phi(\boldsymbol{r}) = \int d^3r\ \phi^*(\boldsymbol{r})\phi(-\boldsymbol{r})$ which is equal to $\int d^3r\ (P\phi)^*(\boldsymbol{r})\,\phi(\boldsymbol{r})$ $= \int d^3r\ \phi^*(-\boldsymbol{r})\phi(\boldsymbol{r})$.

The eigenvalues and eigenfunctions of the parity operator,

$$P\phi_\pi(\boldsymbol{r}) = \pi\,\phi_\pi(\boldsymbol{r}) \tag{88}$$

are $\pi = \pm 1$, both eigenvalues infinitely degenerate. The eigenfunctions corresponding to $\pi = +1$ are the *even* functions, those corresponding to $\pi = -1$ are the *odd* functions.

The proof of this proceeds as follows. On the one hand one has

$$P^2\phi_\pi(\boldsymbol{r}) = \pi\,P\phi_\pi(\boldsymbol{r}) = \pi^2\,\phi_\pi(\boldsymbol{r}),$$

while on the other hand

$$P^2\phi_\pi(\boldsymbol{r}) = P\phi_\pi(-\boldsymbol{r}) = \phi_\pi(\boldsymbol{r}),$$

leading to $\pi^2 = 1$ and $\pi = \pm 1$. Moreover for $\pi = \pm 1$ one has

$$\phi_\pm(-\boldsymbol{r}) = \pm\phi_\pm(\boldsymbol{r}).$$

Next one would like to see what the action is of parity on the operators. Any state ϕ in the Hilbert space is changed into $\phi' = P\phi$, in particular

$$A\phi \longrightarrow PA\phi = \underbrace{PAP^{-1}}_{A'}\,\underbrace{P\phi}_{\phi'},$$

thus

$$A \longrightarrow PAP^{-1}. \tag{89}$$

(Note that for the parity operator actually $P^{-1} = P = P^\dagger$). Examples are

$$\hat{\boldsymbol{r}} \longrightarrow P\hat{\boldsymbol{r}}P^{-1} = -\hat{\boldsymbol{r}}, \tag{90}$$

$$\hat{\boldsymbol{p}} \longrightarrow P\hat{\boldsymbol{p}}P^{-1} = -\hat{\boldsymbol{p}}, \tag{91}$$

$$\hat{\boldsymbol{\ell}} \longrightarrow P\hat{\boldsymbol{\ell}}P^{-1} = +\hat{\boldsymbol{\ell}}, \tag{92}$$

$$\hat{H}(\hat{\boldsymbol{r}},\hat{\boldsymbol{p}}) \longrightarrow P\hat{H}(\hat{\boldsymbol{r}},\hat{\boldsymbol{p}})P^{-1} = \hat{H}(-\hat{\boldsymbol{r}},-\hat{\boldsymbol{p}}). \tag{93}$$

To proof this, e.g. the first relation, one uses that $(\hat{\boldsymbol{r}}\phi)(\boldsymbol{r}) = \boldsymbol{r}\phi(\boldsymbol{r})$ and thus

$$P\hat{\boldsymbol{r}}\phi(\boldsymbol{r}) = P(\hat{\boldsymbol{r}}\phi)(\boldsymbol{r}) = P\boldsymbol{r}\phi(\boldsymbol{r}) = \boldsymbol{r}\,P\phi(\boldsymbol{r}) = \boldsymbol{r}\,\phi(-\boldsymbol{r}) = -\hat{\boldsymbol{r}}\phi(-\boldsymbol{r}),$$

but also

$$P\hat{\boldsymbol{r}}\phi(\boldsymbol{r}) = P\hat{\boldsymbol{r}}P^{-1}P\phi(\boldsymbol{r}) = P\hat{\boldsymbol{r}}P^{-1}\phi(-\boldsymbol{r}).$$

If H is invariant under inversion, one has

$$PHP^{-1} = H \quad \Longleftrightarrow \quad [P,H] = 0. \tag{94}$$

This implies that eigenfunctions of H are also eigenfunctions of P, i.e. they are *even* or *odd*.

10 Examples of inversion symmetry

10.1 Bound states in one dimension

For the one-dimensional hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{d}{dx^2} + V(x), \tag{95}$$

with $V(x) = V(-x)$ we have seen (by explicit calculation) that the solutions separated into two classes, *even* and *odd*. This is a consequence of inversion symmetry, in one dimension only implying $x \longrightarrow -x$. One has correspondingly the definition of parity operator, $P\phi(x) = \phi(-x)$ with *even* and *odd* eigenfunctions. Since a one-dimensional problem has no degeneracy, one always has for a given energy either an even or an odd solutions.

10.2 Particle in a central potential

The hamiltonian for a particle in a central potential is given by

$$H = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(r). \tag{96}$$

One has the following:

- H is invariant under inversion, $\boldsymbol{r} \longrightarrow -\boldsymbol{r}$.
- The eigenfunctions thus have parity $\pi = +$ or $\pi = -$.
- We have already seen what the solutions are for a central potential,

  $$\phi(\boldsymbol{r}) = \frac{u_{n\ell}(r)}{r}\,Y_\ell^m(\theta,\varphi). \tag{97}$$

  and the energy $E_{n\ell}$, independent of the quantum number m. The only part that changes under parity is the angular dependent part,

  $$Y_\ell^m(\theta,\varphi) \;\longrightarrow\; Y_\ell^m(\pi-\theta,\varphi+\pi) = (-)^\ell\,Y_\ell^m(\theta,\varphi). \tag{98}$$

  We see that the parity is already determined by the angular momentum eigenvalue, i.e. $\pi = (-)^\ell$. Thus, although the parity operator can be included in the commuting set of operators for this problem, $\{H, \boldsymbol{\ell}^2, \ell_z, P\}$ (P commutes with all operators in this set), it need not be added explicitly. Note that this certainly is not generally true for the parity operator.

10.3 Electron in atoms

The hamiltonian for Z electrons in atoms is given by

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{Z}\boldsymbol{\nabla}_i^2 + \sum_{i=1}^{Z}\frac{-Ze^2}{4\pi\epsilon_0\,r_i} + \sum_{i>j}^{Z}\frac{e^2}{4\pi\epsilon_0\,|\boldsymbol{r}_i-\boldsymbol{r}_j|}. \tag{99}$$

- Again H is invariant under inversion, $\boldsymbol{r}_i \longrightarrow -\boldsymbol{r}_i$ and the eigenfunctions thus have parity $\pi = +$ or $\pi = -$.
- Without the e-e interaction term the hamiltonian is an example of a separable hamiltonian, the sum of single-electron hydrogen-like hamiltonians, and the eigenfunction thus is the product of the single-electron wave functions (as in Eq. 97),

  $$\phi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_Z) = \prod_{i=1}^{Z}\phi_{n_i\ell_i m_i}(\boldsymbol{r}_i), \tag{100}$$

  $$E = \sum_{i=1}^{Z} E_{n_i\ell_i}, \tag{101}$$

- The parity of this eigenfunctions is

$$\pi = \prod_{i=1}^{Z} \pi_i = \prod_{i=1}^{Z} (-)^{\ell_i} = (-)^{\sum_i \ell_i}. \tag{102}$$

  Be aware of the fact that even though we will later combine the individual angular momenta of the electrons to a total angular momentum L, it still are the individual ℓ_i that determine the parity of an atomic state.

- The electric dipole moment is the operator

$$\boldsymbol{D} = -\sum_i e_i\, \boldsymbol{r}_i. \tag{103}$$

  Its behavior under parity is

$$\boldsymbol{D} \longrightarrow P\boldsymbol{D}P^{-1} = -\boldsymbol{D}. \tag{104}$$

  For parity eigenstates one has vanishing expectation values, $\langle D\rangle = 0$.

  The proof is explicitly given in Mandl without using the parity operator. With the parity operator and the above behavior for $\boldsymbol{D}$ one finds for the expection value of $\boldsymbol{D}$

$$\langle \boldsymbol{D}\rangle = \langle\phi|\boldsymbol{D}|\phi\rangle = \underbrace{\langle\phi|P^{-1}}_{\pi\langle\phi|}\underbrace{P\boldsymbol{D}P^{-1}}_{-\boldsymbol{D}}\underbrace{P|\phi\rangle}_{\pi|\phi\rangle} = -\pi^2\,\langle\phi|\boldsymbol{D}|\phi\rangle = -\langle\boldsymbol{D}\rangle$$

- The electric dipole moment happens to be the (dominant) operator for a photon interacting with the electrons in an atom. Both the absorption of a photon *and* the emission of a photon amounts to acting with the dipole operator on a given initial state $|n_i, \ell_i, m_i\rangle$ (or shorthand $|i\rangle$, where the index i stands for initial). The resulting state $\boldsymbol{D}|i\rangle$ is the new state, which can be expanded in all states available for an electon in the atom. As we have seen before, the probability to find a specific final state $|f\rangle = |n_f, \ell_f, m_f\rangle$ is given by $|\langle f|\boldsymbol{D}|i\rangle|^2$ It is straightforward to derive that

$$\langle f|\boldsymbol{D}|i\rangle = \underbrace{\langle f|P^{-1}}_{\pi_f\langle f|}\underbrace{P\boldsymbol{D}\,P^{-1}}_{-\boldsymbol{D}}\underbrace{P|i\rangle}_{\pi_i|i\rangle} = -\pi_i\pi_f\,\langle f|\boldsymbol{D}|i\rangle, \tag{105}$$

  thus $\langle f|\boldsymbol{D}|i\rangle = 0$ unless $\pi_f = -\pi_i$. Electric dipole transitions are forbidden between states with the same parity. Since parity is determined by the angular momentum of an electron orbit, one sees that it requires $|\Delta\ell| = |\ell_i - \ell_f|$ to be odd. We will see this refined to $|\Delta\ell| = 1$ through rotational symmetry. The above is an example of a *selection rule* and the use of symmetry principles to derive them.

10.4 A diatomic molecule

The hamiltonian for electrons in a diatomic molecule is given by

$$H = -\frac{\hbar^2}{2m}\sum_i \boldsymbol{\nabla}_i^2 + \sum_i \frac{-Z_1e^2}{4\pi\epsilon_0\,|r_i + \boldsymbol{a}|} + \sum_i \frac{-Z_2e^2}{4\pi\epsilon_0\,|r_i - \boldsymbol{a}|} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0\,|\boldsymbol{r}_i - \boldsymbol{r}_j|}. \tag{106}$$

- For $Z_1 = Z_2$ (homonuclear molecules, e.g. N_2 and O_2) inversion is a symmetry, thus the electronic states are parity eigenstates and $\langle\boldsymbol{D}\rangle = 0$.

- For $Z_1 \neq Z_2$ (heteronuclear molecules, e.g. NO) inversion is not a symmetry for the electrons, thus the electronic states are in general not parity eigenstates, allowing the molecule to have a electric dipole moment, $\langle\boldsymbol{D}\rangle \neq 0$.

- Actually for electromagnetic forces *inversion symmetry*, also referred to as *parity invariance* is fundamental. One might then wonder why the existence of electric dipole moments of molecules are allowed. The answer is simple. At the fundamental level parity invariance tells us that the parity inverted world also exists, but this is only achieved by also inverting the positions of the atomic nuclei.

11 Translation symmetry

section 4.2 (Mandl)

Let us start translation symmetry for one dimension,

$$x \longrightarrow x' = x + a. \tag{107}$$

Clearly this is a different kind of symmetry than inversion. There are many more possibilities, in fact infinitely many determined by the continuous parameter a. Translations are an example of *continuous* transformations, while inversion is an example of a *discrete* transformation.

Again we investigate what happens in the Hilbert space of wave functions and we define $\phi \rightarrow \phi' \equiv U(a)\phi$ via

$$\phi'(x') = U(a)\phi(x+a) \equiv \phi(x) \quad \Longrightarrow \quad U(a)\phi(x) = \phi(x-a). \tag{108}$$

For continuous transformations, it turns out to be extremely useful to study first the infinitesimal problem (in general true for socalled Lie transformations). From

$$\phi(x-a) = \phi(x) - a\,\frac{d\phi}{dx} + \ldots,$$

one finds that

$$U(a) = 1 - \frac{i}{\hbar}\,a\,p_x + \ldots. \tag{109}$$

From this infinitesimal behavior one concludes that the translations are *generated* by the momentum operator $p_x = -i\hbar\,\frac{d}{dx}$.

One can extend the above to higher orders,

$$\phi(x-a) = \phi(x) - a\,\frac{d}{dx}\,\phi + \frac{1}{2!}\,a^2\,\frac{d}{dx^2}\,\phi + \ldots,$$

and using the (for operators) definition

$$e^A \equiv 1 + A + \frac{1}{2!}\,A^2 + \ldots,$$

one finds

$$U(a) = \exp\left(-\frac{i}{\hbar}\,a\,p_x\right).$$

In general, if A is a hermitean operator ($A^\dagger = A$), then e^{iA} is a unitary operator ($U^{-1} = U^\dagger$). Thus the shift operator produces new wavefunctions, preserving orthonormality.

Next, we turn to the operators, e.g. the Hamiltonian H. Invariance under translations implies e.g. that $H(x) = H(x+a)$. What does this imply? Just expand infinitesimally,

$$H(x+a) = H(x) + a\,\frac{dH}{dx} + \ldots = H(x) + \frac{i}{\hbar}\,a\,[p_x, H] + \ldots. \tag{110}$$

To see why for operators the commutator appears one should realize that to derive equalities for operators one has to prove that their action on a wave function is the same. A simple check learns that

$$\begin{aligned} [p_x, H]\phi(x) &= p_x(H\phi)(x) - H(p_x\phi)(x) \\ &= -i\hbar\left\{\frac{d}{dx}\,(H(x)\phi(x)) - H(x)\,\frac{d\phi}{dx}\right\} \\ &= -i\hbar\left(\frac{dH}{dx}\right)\phi(x). \end{aligned} \tag{111}$$

The important conclusion is that translation invariance implies

$$H(x+a) = H(x) \iff [p_x, H] = 0. \tag{112}$$

The behavior of the operator under translations can also be obtained in another way. When we use that

$$H(x-a)\phi(x-a) = U(a)\,H(x)\phi(x) = U(a)\,H(x)\,U^{-1}(a)\,\underbrace{U(a)\,\phi(x)}_{\phi(x-a)}, \tag{113}$$

thus

$$H(x-a) = U(a)\,H(x)\,U^{-1}(a), \tag{114}$$

which gives with the infinitesimal form for $U(a)$

$$H(x-a) = \left(1 - \frac{i}{\hbar}\,a\,p_x + \ldots\right) H(x) \left(1 + \frac{i}{\hbar}\,a\,p_x + \ldots\right) = H(x) - \frac{i}{\hbar}\,a\,[p_x, H] + \ldots. \tag{115}$$

A useful (general) relation for operators is the following. Consider operators A, B and H. If H is given by

$$H(c) = e^{cA}\,B\,e^{-cA},$$

where c is a parameter, then

$$\frac{dH}{dc} = e^{cA}\,[A, B]\,e^{-cA}.$$

Translation invariance is generalized to three coordinates of one particle and to more particles by considering

$$\boldsymbol{r}_i \longrightarrow \boldsymbol{r}'_i = \boldsymbol{r}_i + \boldsymbol{a}. \tag{116}$$

The shift operator is

$$\begin{aligned} U(\boldsymbol{a}) &= \exp\left(-\boldsymbol{a}\cdot\sum_i \boldsymbol{\nabla}_i\right) = \exp\left(-\frac{i}{\hbar}\,\boldsymbol{a}\cdot\sum_i \boldsymbol{p}_i\right) = \exp\left(-\frac{i}{\hbar}\,\boldsymbol{a}\cdot\boldsymbol{P}\right) \\ &= 1 - \boldsymbol{a}\cdot\sum_i \boldsymbol{\nabla}_i + \ldots = 1 - \frac{i}{\hbar}\,\boldsymbol{a}\cdot\sum_i \boldsymbol{p}_i + \ldots = 1 - \frac{i}{\hbar}\,\boldsymbol{a}\cdot\boldsymbol{P} + \ldots, \end{aligned} \tag{117}$$

where $\boldsymbol{p}_i = -i\hbar\nabla_i$ are the one-particle momentum operators and $\boldsymbol{P} = \sum_i \boldsymbol{p}_i$ is the *total momentum* operator. Translation invariance implies that

$$U(\boldsymbol{a})\,H\,U^{-1}(\boldsymbol{a}) = H \iff [\boldsymbol{P}, H] = 0. \tag{118}$$

12 Examples of translation symmetry

12.1 Free particle

The single-particle hamiltonian

$$H = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\boldsymbol{r})$$

is in general not invariant under translations. The first term is invariant, but the second only if $V(\boldsymbol{r}) =$ constant. Shifting the zeropoint of the energy one has $H = -\hbar^2\boldsymbol{\nabla}^2/2m$, i.e. a free particle. Indeed one then has

$$[\boldsymbol{p}, H] = 0,$$

and the eigenstates of the momentum operator

$$\phi_p(\boldsymbol{r}) = \sqrt{\rho}\,\exp\left(i\,\boldsymbol{p}\cdot\boldsymbol{r}/\hbar\right),$$

indeed coincide with eigenstates of the hamiltonian, with $E = p^2/2m$.

12.2 Two-particle system

The two-particle system with the hamiltonian

$$H = \frac{\boldsymbol{p}_1^2}{2m_1} + \frac{\boldsymbol{p}_2^2}{2m_2} + V(\boldsymbol{r}_1 - \boldsymbol{r}_2) \tag{119}$$

is invariant under translations. This means that $[\boldsymbol{P}, H] = 0$, where $\boldsymbol{P} = \boldsymbol{p}_1 + \boldsymbol{p}_2$. For this hamiltonian, we indeed have seen that introducing center of mass and relative coordinates a separation of the hamiltonian is obtained,

$$H = \frac{\boldsymbol{P}^2}{2M} + \frac{\boldsymbol{p}^2}{2\mu} + V(\boldsymbol{r}) \tag{120}$$

with $\boldsymbol{P} = \boldsymbol{p}_1 + \boldsymbol{p}_2$. The commutation relation implies common eigenfunctions of the hamiltonian and the total momentum operator. Since $\boldsymbol{P} = -i\hbar\,\boldsymbol{\nabla}_R$, these are the functions

$$\phi_P(\boldsymbol{R}) \propto \exp\left(\frac{i}{\hbar}\,\boldsymbol{P}\cdot\boldsymbol{R}\right).$$

Thus for the hamiltonian we deduce from tranlation invariance that the wave function must be of the form

$$\phi(\boldsymbol{R}, \boldsymbol{r}) = e^{i\,\boldsymbol{P}\cdot\boldsymbol{R}/\hbar}\,\phi_{\rm rel}(\boldsymbol{r}).$$

13 Rotation symmetry

section 4.3 (Mandl)

Rotations are characterized by a rotation axis and an angle,

$$\boldsymbol{r} \longrightarrow R(\hat{n},\alpha)\,\boldsymbol{r}, \tag{121}$$

e.g. for a rotation around the z-axis one has explicitly

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \longrightarrow \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{122}$$

As for other symmetry transformations, this gives rise to a unitary transformation in the Hilbert space of wave functions $\phi \to \phi' \equiv U(\hat{n},\alpha)\,\phi$,

$$U(\hat{n},\alpha)\,\phi\,(R(\hat{n},\alpha)\boldsymbol{r}) = \phi(\boldsymbol{r}) \quad\Longrightarrow\quad U(\hat{n},\alpha)\,\phi(\boldsymbol{r}) = \phi\left(R^{-1}(\hat{n},\alpha)\boldsymbol{r}\right). \tag{123}$$

For a rotation around the z-axis it is convenient to use polar coordinates,

$$U(\hat{z},\alpha)\,\phi(r,\theta,\varphi) = \phi(r,\theta,\varphi-\alpha). \tag{124}$$

Using

$$\begin{aligned} \phi(r,\theta,\varphi-\alpha) &= \phi(r,\theta,\varphi) - \alpha\,\frac{\partial}{\partial\varphi}\,\phi + \ldots \\ &= \left(1 - \frac{i}{\hbar}\,\alpha\left(-i\hbar\,\frac{\partial}{\partial\varphi}\right) + \ldots\right)\phi \\ &= \left(1 - \frac{i}{\hbar}\,\alpha\,\ell_z + \ldots\right)\phi, \end{aligned} \tag{125}$$

one finds that ℓ_z is the generator of rotations around the z-axis, and

$$U(\hat{z},\alpha) = \exp\left(-\frac{i}{\hbar}\,\alpha\,\ell_z\right) = 1 - \frac{i}{\hbar}\,\alpha\,\ell_z + \ldots\ . \tag{126}$$

As for the translations, the operator behaves as

$$\begin{aligned} H(r,\theta,\varphi-\alpha) &= H(r,\theta,\varphi) - \alpha\,\frac{\partial H}{\partial\varphi} + \ldots \\ &= H - \frac{i}{\hbar}\,\alpha\,[\ell_z, H] + \ldots \\ &= U(\hat{z},\alpha)\,H\,U^{-1}(\hat{z},\alpha). \end{aligned} \tag{127}$$

Rotational invariance (around z-axis) implies that

$$U(\hat{z},\alpha)\,H\,U^{-1}(\hat{z},\alpha) = H \iff [\boldsymbol{\ell}_z, H] = 0. \tag{128}$$

Although the situation looks quite similar to the translations, there is an important difference. For two consecutive rotations the order is important (rotations do not commute)

$$\begin{aligned} R(\hat{x},\alpha)\,R(\hat{y},\beta) &\neq R(\hat{y},\beta)\,R(\hat{x},\alpha), \\ U(\hat{x},\alpha)\,U(\hat{y},\beta) &\neq U(\hat{y},\beta)\,U(\hat{x},\alpha). \end{aligned}$$

For the rotations in the Hilbert space, this is already evident from the infinitesimal rotations. The generators do not commute,

$$[\ell_x, \ell_y] = i\hbar\,\ell_z,$$

etc.

A general relation for operators is

$$e^{A}\,e^{B}=e^{C}\quad\text{with}\quad C=A+B+[A,B]+\frac{1}{2!}[A,[A,B]]+\dots\ .$$

(Baker-Campbell-Hausdorff relation)

For more particles, invariance under rotations implies

$$H\text{ invariant}\Longleftrightarrow[\boldsymbol{L},H]=0, \tag{129}$$

where $\boldsymbol{L}=\sum_i\boldsymbol{\ell}_i$. This is a fundamental symmetry of nature for particles without spin!

14 Examples of rotation symmetry

14.1 One particle in a central potential

Already in chapter 2 of Mandl we have seen the treatment of a particle in a central potential,

$$H = -\frac{\hbar^2}{2m}\,\boldsymbol{\nabla}^2 + V(r)$$

One has rotation invariance and thus $[\boldsymbol{\ell}, H] = 0$ for all three generators of rotations. This provides us with a number of candidates for the wanted set of commuting operators. Because the three angular momentum operators do not commute among themselves, we have to make a choice. We already have seen that in this case this leads for instance to the choice $\{H, \boldsymbol{\ell}^2, \ell_z\}$, on the basis of which one could conclude that the eigenfunctions of the hamiltonian could be written as

$$\phi_{n\ell m}(\boldsymbol{r}) = \frac{u_{n\ell m}(r)}{r}\,Y_\ell^m(\theta, \varphi).$$

That the index m is irrelevant for the above hamiltonian can not be deduced from symmetry considerations.

14.2 Two-particle system

For the two-particle hamiltonian of Eq. 119 one can in the case that $V(\boldsymbol{r}_1 - \boldsymbol{r}_2) = V(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)$, add invariance under rotations in the relative coordinate to deduce *without doing any explicit calculations* that the solution must be of the form

$$\phi(\boldsymbol{R}, \boldsymbol{r}) = e^{i\,\boldsymbol{P}\cdot\boldsymbol{R}/\hbar}\,\frac{u_{nlm}(r)}{r}\,Y_\ell^m(\theta, \varphi).$$

14.3 The diatomic molecule

We return to the case of the diatomic molecule.

- The diatomic molecule is only invariant under rotations around the z-axis, i.e. $[H, \ell_z] = 0$, but $[H, \boldsymbol{\ell}^2] \neq 0$. Solutions thus can be labeled as $\phi_m \propto e^{im\varphi}$. It is easy to see by rewriting the gradient in cilinder coordinates that the solutions with opposite m-values are degenerate (only ℓ_z^2 appears in the hamiltonian) since

  $$-\hbar^2\boldsymbol{\nabla}^2 = -\hbar^2\frac{\partial^2}{\partial z^2} - \hbar^2\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\,\frac{\partial}{\partial\rho}\right) + \frac{\ell_z^2}{\rho^2},$$

  where $\rho^2 = x^2 + y^2$.

- The diatomic (heteronuclear) molecule is not invariant under parity. But an interesting operator is

  $$P_{xz}\phi(x, y, z) = \phi(x, -y, z) \tag{130}$$

  (mirror symmetry in the xz-plane). This is a symmetry of the hamiltonian and thus $[P_{xz}, H] = 0$.

- We note that ℓ_z does not commute with P_{xz}, but knowing that $\ell_z = xp_y - yp_x$ we have $P_{xz}\,\ell_z\,P_{xz}^{-1} = -\ell_z$. Note that $[\ell_z^2, P_{xz}] = 0$.

- This implies that there are two possibilities

  $$P_{xz}\phi_m = \pm\phi_{-m}.$$

  This is easily proven by using $\ell_z\,P_{xz}\phi_m = -P_{xz}\,\ell_z\,P_{xz}^{-1}\,P_{xz}\phi_m = -P_{xz}\,\ell_z\,\phi_m = -m\hbar\,P_{xz}\phi_m$ and $P_{xz}^2 = 1$.

- Thus for $m = 0$ one has either ϕ_{0+} *or* ϕ_{0-}, while for $m \neq 0$ one has two solutions $\phi_{|m|\pm} \propto (\phi_m \pm \phi_{-m})$, solutions referred to as *gerade* (+) or *ungerade* (-).

15 Identical particles

section 4.4 (Mandl)

The hamiltonian for Z electrons in an atom,

$$H(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_Z;\boldsymbol{p}_1,\ldots,\boldsymbol{p}_Z) = \sum_{i=1}^{Z}\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}_i^2 - \frac{Ze^2}{4\pi\epsilon_0\, r_i}\right) + \sum_{i>j}^{Z}\frac{e^2}{4\pi\epsilon_0\,|\boldsymbol{r}_i-\boldsymbol{r}_j|}$$

is invariant under *permutations* of the particle labels, $i \leftrightarrow j$, written symbolically as

$$H(1\ldots i\ldots j\ldots Z) = H(1\ldots j\ldots 1\ldots Z). \tag{131}$$

Consider first two identical particles and assume an eigenstate $\phi(12)$,

$$H(12)\phi(12) = E\phi(12),$$

Because $H(12) = H(21)$ one has also

$$H(21)\phi(12) = E\phi(12).$$

Since the labeling is arbitrary one can rewrite the latter to

$$H(12)\phi(21) = E\phi(21).$$

Thus there are two degenerate solutions $\psi(1,2)$ and $\psi(2,1)$. In particular we can choose symmetric and antisymmetric combinations

$$\phi^{S/A} = \phi(12) \pm \phi(21), \tag{132}$$

which are also eigenstates with the same energy. These are eigenfunctions of the permutation operator P_{ij}, which interchanges two labels, i.e. $P_{ij}\phi(1\ldots i\ldots j\ldots) = \phi(1\ldots j\ldots i\ldots)$ with eigenvalues + and - respectively. This operator commutes with H and the symmetry is not changed in time.

For three particles one has six degenerate solutions, $\phi(123)$, $\phi(213)$, $\phi(231)$, $\phi(321)$, $\phi(312)$ and $\phi(132)$. There is one totally symmetric combination,

$$\phi^S = \phi(123) + \phi(213) + \phi(231) + \phi(321) + \phi(312) + \phi(132) \tag{133}$$

(any permutation operator gives back the wave function), one totally antisymmetric combination

$$\phi^S = \phi(123) - \phi(213) + \phi(231) - \phi(321) + \phi(312) - \phi(132) \tag{134}$$

(any permutation operator gives back minus the wave function) and there are four combinations with mixed symmetry. Nature is kind and only uses the *symmetric* wave functions (for *bosons*) or the *antisymmetric* wave function (for *fermions*). Bosons are particles with integer spin, fermions with half-integer spin (we come to this back after this section).

For instance for electrons which have spin 1/2 (two possible spin states) the total wave function must be antisymmetric. This has profound consequences. It underlies the periodic table of elements. Consider again for simplicity a two-particle system which neglecting mutual interactions has a separable hamiltonian of the form

$$H = H_0(1) + H_0(2).$$

Suppose the solutions of the single-particle hamiltonian are known,

$$H_0(1)\phi_a(1) = E_a\phi_a(1), H_0(1)\phi_b(1) = E_b\phi_b(1),$$

etc. Considering the lowest two single-particle states available, there are three symmetric states and one anti-symmetric state,

$$\begin{array}{rl} \text{symmetric:} & \left\{\begin{array}{l} \phi_a(1)\,\phi_a(2) \\ \phi_a(1)\,\phi_b(2) + \phi_b(1)\,\phi_a(2) \\ \phi_b(1)\,\phi_b(2) \end{array}\right. \\ \text{antisymmetric:} & \phi_a(1)\,\phi_b(2) - \phi_b(1)\,\phi_a(2) \end{array}$$

In particular bosons can all reside in the lowest state, while any two fermions cannot be in the same state (*Pauli exclusion principle*).

A way to obtain the completely antisymmetric wave function is by constructing the antisymmetric wave function as a *Slater determinant*, for instance for three particles the antisymmetric wave function constructed from three available states ϕ_a, ϕ_b and ϕ_c is

$$\phi^A(123) = \frac{1}{\sqrt{3!}} \left| \begin{array}{c} \phi_a(1)\phi_a(2)\phi_a(3) \\ \phi_b(1)\phi_b(2)\phi_b(3) \\ \phi_c(1)\phi_c(2)\phi_c(3) \end{array} \right| .$$

The most well-known application is the consecutive filling of atomic levels $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $\ldots$, giving the periodic table of elements. The available states for each of the levels is $2(2\ell+1)$ accounting for the spin-degeneracy and the ℓ-degeneracy.

16 Spin

16.1 Definition

In quantum mechanics spin is introduced as an observable defined via the vector operator $\boldsymbol{s}$. These (three) hermitean operators satisfy commutation relations

$$[s_i, s_j] = i\hbar\epsilon_{ijk}\, s_k, \tag{135}$$

similar to the commutation relations for the angular momentum operator $\boldsymbol{\ell} = \boldsymbol{r} \times \boldsymbol{p}$. The spin operators $\boldsymbol{s}$ commute with the operators $\boldsymbol{r}$ and $\boldsymbol{p}$ and thus also with $\boldsymbol{\ell}$. That's it. All the rest follows from these commutation relations.

16.2 Rotation invariance

Earlier we have seen that, without spin, rotation invariance required specific commutation relations with $\boldsymbol{\ell}$. In fact *scalar* quantities S and *vectors* $\boldsymbol{V}$ under rotations behaved like

$$[\ell_i, S] = 0, \tag{136}$$

$$[\ell_i, V_j] = i\hbar\, \epsilon_{ijk}\, V_k, \tag{137}$$

e.g. scalars $S = \boldsymbol{r}^2$, $\boldsymbol{p}^2$, $\boldsymbol{r}\cdot\boldsymbol{p}$ or $\boldsymbol{\ell}^2$ and vectors $\boldsymbol{V} = \boldsymbol{r}$, $\boldsymbol{p}$ or $\boldsymbol{\ell}$.

Including spin vectors $\boldsymbol{s}$, the notion of behavior under rotations has to be altered, e.g. $[\ell_i, s_j] = 0$ and $[\ell_i, \boldsymbol{\ell}\cdot\boldsymbol{s}] = -i\hbar\,(\boldsymbol{\ell}\times\boldsymbol{s})_i$. It is easy to see that the operator

$$\boldsymbol{j} \equiv \boldsymbol{\ell} + \boldsymbol{s}, \tag{138}$$

satisfies

$$[j_i, S] = 0, \tag{139}$$

$$[j_i, V_j] = i\hbar\, \epsilon_{ijk}\, V_k, \tag{140}$$

not only for the above examples, but now also for the vectors $\boldsymbol{s}$ and $\boldsymbol{j}$ and including scalars like $\boldsymbol{s}^2$ and $\boldsymbol{\ell}\cdot\boldsymbol{s}$.

For a system of many particles the operators $\boldsymbol{r}$, $\boldsymbol{p}$ and $\boldsymbol{s}$ for different particles commute. It is easy to see that the operators

$$\boldsymbol{L} = \sum_{n=1}^{N} \boldsymbol{\ell}_n, \qquad \boldsymbol{S} = \sum_{n=1}^{N} \boldsymbol{s}_n, \qquad \boldsymbol{J} = \sum_{n=1}^{N} \boldsymbol{j}_n = \boldsymbol{L} + \boldsymbol{S}, \tag{141}$$

satisfy commutation relations $[L_i, L_j] = i\hbar\,\epsilon_{ijk}\, L_k$, $[S_i, S_j] = i\hbar\,\epsilon_{ijk}\, S_k$, and $[J_i, J_j] = i\hbar\,\epsilon_{ijk}\, J_k$, while only the operator $\boldsymbol{J}$ satisfies

$$[J_i, S] = 0, \tag{142}$$

$$[J_i, V_j] = i\hbar\, \epsilon_{ijk}\, V_k, \tag{143}$$

for any scalar S or vector $\boldsymbol{V}$.

> *It is easy to show that the inner product $\boldsymbol{a}\cdot\boldsymbol{b}$ of two vectors satisfying the commutation relation in Eq. 143 indeed is a scalar quantity, satifying the commutation relation in Eq. 142.*

An important property is that rotational invariance is one of the basic symmetries of our world.

Rotation invariance of a system of particles requires

$$\boxed{[\boldsymbol{J}, H] = 0.} \tag{144}$$

Besides the behavior under rotations, also the behavior under parity is considered to classify quantities. Vectors behave as $P\,\boldsymbol{V}\,P^{-1} = -\boldsymbol{V}$, *axial vectors as* $P\,\boldsymbol{A}\,P^{-1} = +\boldsymbol{A}$, *a scalar* S *behave as* $P\,S\,P^{-1} = +S$, *and a pseudoscalar* S' *behaves as* $P\,S'\,P^{-1} = -S'$. *Examples of specific quantities are*

vector	*axial vector*	*scalar*	*pseudoscalar*
$\boldsymbol{r}$	$\boldsymbol{\ell}$	$\boldsymbol{r}^2$	$\boldsymbol{s}\cdot\boldsymbol{r}$
$\boldsymbol{p}$	$\boldsymbol{s}$	$\boldsymbol{p}^2$	$\boldsymbol{s}\cdot\boldsymbol{p}$
	$\boldsymbol{j}$	$\boldsymbol{\ell}^2$	
		$\boldsymbol{\ell}\cdot\boldsymbol{s}$	

The hamiltonian is a scalar quantity. Therefore, if we have parity invariance, combinations as $\boldsymbol{s}\cdot\boldsymbol{r}$ *cannot appear but a tensor operator of the form* $(\boldsymbol{s}_1\cdot\boldsymbol{r})(\boldsymbol{s}_2\cdot\boldsymbol{r})$ *is allowed. Note, however, that such an operator does not commute with* $\boldsymbol{\ell}$ *(see Exc. 5.8).*

16.3 spin states

As mentioned above, the commutation relations are all that defines spin. As an operator that commutes with all three spin operators (a socalled Casimir operator) we have $\boldsymbol{s}^2 = s_x^2 + s_y^2 + s_z^2$,

$$[s_i, s_j] = i\hbar\,\epsilon_{ijk}\,s_k, \tag{145}$$

$$[\boldsymbol{s}^2, s_i] = 0. \tag{146}$$

Only one of the three spin operators can be used to label states, for which we without loss of generality can take s_z. In addition we can use $\boldsymbol{s}^2$, which commutes with s_z. We write states $\chi_m^{(s)} = |s,m\rangle$ satisfying

$$\boldsymbol{s}^2|s,m\rangle = \hbar^2\,s(s+1)|s,m\rangle, \tag{147}$$

$$\boldsymbol{s}_z|s,m\rangle = m\hbar\,|s,m\rangle. \tag{148}$$

It is of course a bit premature to take $\hbar^2\,s(s+1)$ as eigenvalue. We need to prove that the eigenvalue of $\boldsymbol{s}^2$ is positive, but this is straightforward as it is the sum of three squared operators. Since the spin operators are hermitean each term is not just a square but also the product of the operator and its hermitean conjugate. In the next step, we recombine the operators s_x and s_y into

$$s_\pm \equiv s_x \pm i\,s_y. \tag{149}$$

The commutation relations for these operators are,

$$[\boldsymbol{s}^2, s_\pm] = 0, \tag{150}$$

$$[s_z, s_\pm] = \pm\hbar\,s_\pm, \tag{151}$$

$$[s_+, s_-] = 2\hbar\,s_z, \tag{152}$$

The first two can be used to show that

$$\boldsymbol{s}^2\,s_\pm|s,m\rangle = s_\pm\boldsymbol{s}^2|s,m\rangle = \hbar^2\,s(s+1)\,s_\pm|s,m\rangle,$$
$$s_z\,s_\pm|s,m\rangle = (s_\pm s_z \pm \hbar\,s_\pm)\,|s,m\rangle = (m\pm 1)\hbar\,s_\pm|s,m\rangle,$$

hence the name step-operators (raising and lowering operator) which achieve

$$s_\pm|s,m\rangle = c_\pm|s,m\pm 1\rangle.$$

Furthermore we have $s_\pm^\dagger = s_\mp$ and $\boldsymbol{s}^2 = s_z^2 + (s_+s_- + s_-s_+)/2$, from which one finds that

$$\begin{aligned} |c_\pm|^2 = \langle s,m|s_\pm^\dagger s_\pm|s,m\rangle &= \langle s,m|\boldsymbol{s}^2 - s_z^2 - [s_\pm, s_\mp]/2|s,m\rangle \\ &= \langle s,m|\boldsymbol{s}^2 - s_z^2 \mp \hbar\,s_z|s,m\rangle = s(s+1) - m(m\pm 1). \end{aligned}$$

It is convention to define

$$\begin{aligned} s_+|s,m\rangle &= \hbar\sqrt{s(s+1)-m(m+1)}\,|s,m+1\rangle \\ &= = \hbar\sqrt{(s-m)(s+m+1)}\,|s,m+1\rangle \qquad (153) \\ s_-|s,m\rangle &= \hbar\sqrt{s(s+1)-m(m-1)}\,|s,m-1\rangle \\ &= \hbar\sqrt{(s+m)(s-m+1)}\,|s,m-1\rangle. \qquad (154) \end{aligned}$$

This shows that given a state $|s,m\rangle$, we have a whole series of states

$$\ldots |s,m-1\rangle,\ |s,m\rangle,\ |s,m+1\rangle, \ldots$$

But, we can also easily see that since $\boldsymbol{s}^2 - s_z^2 = s_x^2 + s_y^2$ must be an operator with positive definite eigenstates that $s(s+1) - m^2 \geq 0$, i.e. $|m| \leq \sqrt{s(s+1)}$ or strictly $|m| < s+1$. From the second expressions in Eqs 153 and 154 one sees that this inequality requires $m_{max} = s$ as one necessary state to achieve a cutoff of the series of states on the upper side, while $m_{min} = -s$ is required as a necessary state to achieve a cutoff of the series of states on the lower side. Moreover to have both cutoffs the step operators require that the difference $m_{max} - m_{min} = 2\,s$ must be an integer, i.e. the only allowed values of spin quantum numbers are

$$\begin{aligned} s &= 0,\ 1/2,\ 1,\ 3/2, \ldots, \\ m &= s, s-1, \ldots, -s. \end{aligned}$$

Thus for spin states with a given quantum number s, there exist $2s+1$ states.

16.4 Why is ℓ integer

Purely on the basis of the commutation relations, the allowed values for the quantum numbers s and m have been derived. Since the angular momentum operators $\boldsymbol{\ell} = \boldsymbol{r} \times \boldsymbol{p}$ satisfy the same commutation relations, one has the same restrictions on ℓ and m_ℓ, the eigenvalues connected with $\boldsymbol{\ell}^2$ and ℓ_z. However, we have only found integer values for the quantum numbers in our earlier treatment. This is the consequence of restrictions imposed because for $\boldsymbol{\ell}$ we know *more* than just the commutation relations. The operators have been introduced explicitly working in the space of functions, depending on the angles in R^3. One way of seeing where the constraint is coming from is realizing that we want uni-valued functions. The eigenfunctions of $\ell_z = -i\hbar\, d/d\phi$, were found to be

$$Y_\ell^m(\theta,\phi) \propto e^{i\,m\phi}.$$

In order to have the same value for ϕ and $\phi + 2\pi$ we need $\exp(2\pi\, i\, m) = 1$, hence m (and thus also ℓ) can only be integer.

For spin, there are only the commutation relations, thus the spin quantum numbers s can also take half-integer values. Particles with integer spin values are called *bosons* (e.g. pions, photons), particles with half-integer spin values are called *fermions* (e.g. electrons, protons, neutrinos, quarks). For the angular momenta which are obtained as the sum of other operators, e.g. $\boldsymbol{j} = \boldsymbol{\ell} + \boldsymbol{s}$, etc. one can easily see what is allowed. Because the z-components are additive, one sees that for any orbital angular momentum the quantum numbers are integer, while for spin and total angular momentum integer and half-integer are possible.

17 Spin states

17.1 Matrix representations of spin operators

In the space of spin states with a given quantum number s, we can write the spin operators as $(2s+1) \times (2s+1)$ matrices. Let us illustrate this first for spin $s = 1/2$. Define the states

$$\chi^{(1/2)}_{+1/2} \quad \text{or} \quad \chi_{\uparrow} \quad \text{or} \quad |1/2,+1/2\rangle \equiv \left(\begin{array}{c} 1 \\ 0 \end{array} \right),$$

$$\chi^{(1/2)}_{-1/2} \quad \text{or} \quad \chi_{\downarrow} \quad \text{or} \quad |1/2,-1/2\rangle \equiv \left(\begin{array}{c} 0 \\ 1 \end{array} \right).$$

Using the definition of the quantum numbers in Eq. 148 one finds that

$$s_z = \hbar \left(\begin{array}{cc} 1/2 & 0 \\ 0 & -1/2 \end{array} \right), \quad s_+ = \hbar \left(\begin{array}{cc} 0 & 0 \\ 1 & 0 \end{array} \right), \quad s_- = \hbar \left(\begin{array}{cc} 0 & 1 \\ 0 & 0 \end{array} \right),$$

For spin 1/2 we find the familiar spin matrices, $\boldsymbol{s} = \hbar\boldsymbol{\sigma}/2$,

$$\sigma_x = \left(\begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array} \right), \quad \sigma_y = \left(\begin{array}{cc} 0 & -i \\ i & 0 \end{array} \right), \quad \sigma_z = \left(\begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right).$$

For spin 1 we define the basis states,

$$\chi^{(1)}_{+1} = |1,+1\rangle \equiv \left(\begin{array}{c} 1 \\ 0 \\ 0 \end{array} \right), \quad \chi^{(1)}_{0} = |1,0\rangle \equiv \left(\begin{array}{c} 0 \\ 1 \\ 0 \end{array} \right), \quad \chi^{(1)}_{-1} = |1,0\rangle \equiv \left(\begin{array}{c} 0 \\ 0 \\ 1 \end{array} \right).$$

The spin matrices are then easily found,

$$s_z = \hbar \left(\begin{array}{ccc} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{array} \right), \quad s_+ = \hbar \left(\begin{array}{ccc} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{array} \right), \quad s_- = \hbar \left(\begin{array}{ccc} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{array} \right),$$

from which also s_x and s_y can be constructed.

17.2 Rotated spin states

Instead of the spin states defined as eigenstates of s_z, one might be interested in eigenstates of $\boldsymbol{s} \cdot \hat{\boldsymbol{n}}$, e.g. because one wants to measure it with a Stern-Gerlach apparatus with an inhomogeneous $\boldsymbol{B}$-field in the $\hat{\boldsymbol{n}}$ direction. We can of course just write down these states formally like

$$\chi^{(1/2)}_{+1/2}(\hat{\boldsymbol{n}}) \quad \text{and} \quad \chi^{(1/2)}_{-1/2}(\hat{\boldsymbol{n}})$$

Suppose that we want to write them down in terms of the eigenstates of s_z, given above. To do this we work in the matrix representation discussed in the previous section. Taking $\hat{\boldsymbol{n}} = (\sin\theta, 0, \cos\theta)$, we can easily write down

$$\boldsymbol{s} \cdot \hat{\boldsymbol{n}} = \frac{1}{2}\hbar\,\boldsymbol{\sigma} \cdot \hat{\boldsymbol{n}} = \frac{\hbar}{2} \left(\begin{array}{cc} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{array} \right). \tag{155}$$

We find the following two eigenstates and eigenvalues

$$\chi^{(1/2)}_{+1/2}(\hat{\boldsymbol{n}}) = \left(\begin{array}{c} \cos(\theta/2) \\ \sin(\theta/2) \end{array} \right) \quad \text{with eigenvalue} \quad +1/2,$$

$$\chi^{(1/2)}_{-1/2}(\hat{\boldsymbol{n}}) = \left(\begin{array}{c} -\sin(\theta/2) \\ \cos(\theta/2) \end{array} \right) \quad \text{with eigenvalue} \quad -1/2.$$

The probability that given a state with spin along the z-direction a measurement of the spin along the $+\hat{\boldsymbol{n}}$-direction yields the value $+\hbar/2$ is thus given by

$$\left| \chi^{(1/2)\,\dagger}_{+1/2}(\hat{\boldsymbol{n}})\chi^{(1/2)}_{+1/2} = \right|^2 = \cos^2(\theta/2).$$

In general the rotated eigenstates are written as

$$\chi_m^{(s)}(\hat{\boldsymbol{n}}) = \begin{pmatrix} d_{sm}^{(s)}(\theta) \\ \vdots \\ d_{m'm}^{(s)}(\theta) \\ \vdots \\ d_{-sm}^{(s)}(\theta) \end{pmatrix}. \tag{156}$$

where $d_{m'm}(\theta)$ *are the d-functions. These are in fact just matrix elements of the spin rotation matrix* $\exp(-i\,\theta\,S_y)$ *between states quantized along the z-direction. Extended to include azimuthal dependence it is customary to use the rotation matrix* $e^{-i\,\phi\,S_z}\,e^{-i\,\theta\,S_y}\,e^{-i\,\chi\,S_3}$ *and the functions are called* $D_{m'm}(\phi,\theta,\chi)$*.*

18 Combination of angular momenta

18.1 Quantum number analysis

We consider situations in which two sets of angular momentum operators play a role, e.g.

- An electron with spin in an atomic ($n\ell$)-orbit (spin $\boldsymbol{s}$ and orbital angular momentum $\boldsymbol{\ell}$ combined into a total angular momentum $\boldsymbol{j} = \boldsymbol{\ell} + \boldsymbol{s}$).
- Two electrons with spin (spin operators $\boldsymbol{s}_1$ and $\boldsymbol{s}_2$, combined into $\boldsymbol{S} = \boldsymbol{s}_1 + \boldsymbol{s}_2$).
- Two electrons in atomic orbits (orbital angular momenta $\boldsymbol{\ell}_1$ and $\boldsymbol{\ell}_2$ combined into total orbital angular momentum $\boldsymbol{L} = \boldsymbol{\ell}_1 + \boldsymbol{\ell}_2$).
- Combining the total orbital angular momentum of electrons in an atom ($\boldsymbol{L}$) and the total spin ($\boldsymbol{S}$) into the total angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$.

Let us discuss as the generic example

$$\boldsymbol{J} = \boldsymbol{j}_1 + \boldsymbol{j}_2. \tag{157}$$

We have states characterized by the direct product of two states,

$$|j_1, m_1\rangle \otimes |j_2, m_2\rangle, \tag{158}$$

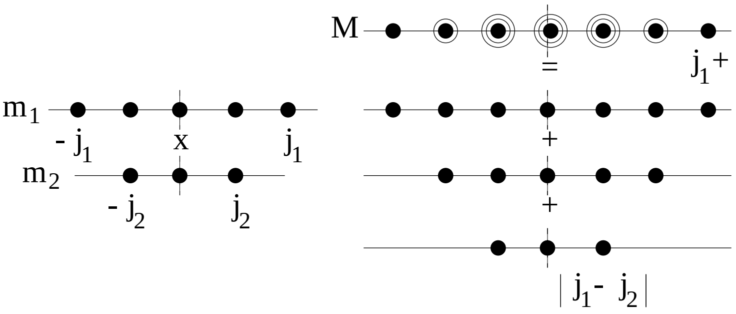
which we can write down since not only $[\boldsymbol{j}_1^2, j_{1z}] = [\boldsymbol{j}_2^2, j_{2z}] = 0$, but also $[j_{1m}, j_{2n}] = 0$. The sum-operator $\boldsymbol{J}$ obviously is not independent, but since the $\boldsymbol{J}$-operators again satisfy the well-known angular momentum commutation relations we can look for states characterized by the commuting operators $\boldsymbol{J}^2$ and J_z, $|\ldots; J, M\rangle$. It is easy to verify that of the four operators characterizing the states in Eq. 158, $[\boldsymbol{J}^2, j_{1z}] \neq 0$ and $[\boldsymbol{J}^2, j_{2z}] \neq 0$ (Note that $\boldsymbol{J}^2$ contains the operator combination $2\boldsymbol{j}_1 \cdot j_2$, which contains operators like j_{1x}, which do not commute with j_{1z}). It is easy to verify that one does have

$$\begin{aligned}
&[\boldsymbol{J}^2, \boldsymbol{j}_1^2] = [\boldsymbol{J}^2, \boldsymbol{j}_2^2] = 0, \\
&[J_z, \boldsymbol{j}_1^2] = [J_z, \boldsymbol{j}_2^2] = 0,
\end{aligned}$$

and thus we can relabel the $(2j_1+1)(2j_2+1)$ states in Eq. 158 into states characterized with the quantum numbers

$$|j_1, j_2; J, M\rangle. \tag{159}$$

The basic observation in the relabeling is that $J_z = j_{1z} + j_{2z}$ and hence $M = m_1 + m_2$. This leads to the following scheme, in which in the left part the possible m_1 and m_2-values are given and the upper right part the possible sum-values for M including their degeneracy.



1. Since $|m_1| \leq j_1$ and $|m_2| \leq j_2$, the maximum value for M is $j_1 + j_2$. This state is unique.
2. Since $J_+ = j_{1+} + j_{2+}$ acting on this state is zero, it corresponds to a state with $J = j_1 + j_2$. Then, there must exist other states (in total $2J+1$), which can be constructed via $J_- = j_{1-} + j_{2-}$ (in the scheme indicated as the first set of states in the right part below the equal sign).

3. In general the state with $M = j_1 + j_2 - 1$ is twofold degenerate. One combination must be the state obtained with J_- from the state with $M = j_1 + j_2$, the other must be orthogonal to this state and again represents a 'maximum M'-value corresponding to $J = j_1 + j_2 - 1$.
4. This procedure goes on till we have reached $M = |j_1 - j_2|$, after which the degeneracy is equal to the $\min\{2j_1 + 1, 2j_2 + 1\}$, and stays constant till the M-value reaches the corresponding negative value.

Thus

Combining two angular momenta j_1 and j_2 we find resulting angular momenta J with values

$$J = j_1 + j_2,\ j_1 + j_2 - 1, \ldots, |j_1 - j_2|, \tag{160}$$

going down in steps of one.

Note that the total number of states is (as expected)

$$\sum_{J=|j_1-j_2|}^{j_1+j_2} (2J+1) = (2j_1+1)(2j_2+1). \tag{161}$$

Furthermore we have in combining angular momenta:

half-integer with half-integer	$\longrightarrow$	integer
integer with half-integer	$\longrightarrow$	half-integer
integer with integer	$\longrightarrow$	integer

18.2 Clebsch-Gordon coefficients

The actual construction of states just follows the steps outlined above. Let us illustrate it for the case of combining two spin 1/2 states. We have four states according to labeling in Eq. 158,

$$\begin{aligned}
|s_1, m_1\rangle \otimes |s_2, m_2\rangle : \qquad & |1/2, +1/2\rangle \otimes |1/2, +1/2\rangle \equiv |\uparrow\uparrow\rangle, \\
& |1/2, +1/2\rangle \otimes |1/2, -1/2\rangle \equiv |\uparrow\downarrow\rangle, \\
& |1/2, -1/2\rangle \otimes |1/2, +1/2\rangle \equiv |\downarrow\uparrow\rangle, \\
& |1/2, -1/2\rangle \otimes |1/2, -1/2\rangle \equiv |\downarrow\downarrow\rangle.
\end{aligned}$$

1. The highest state has $M = 1$ and must be the first of the four states above. Thus for the labeling $|s_1, s_2; S, M\rangle$

$$|1/2, 1/2; 1, +1\rangle = |\uparrow\uparrow\rangle. \tag{162}$$

2. Using $S_- = s_{1-} + s_{2-}$ we can construct the other $S + 1$ states.

$$\begin{aligned}
&S_-|1/2, 1/2; 1, +1\rangle = \hbar\,\sqrt{2}\,|1/2, 1/2; 1, 0\rangle, \\
&(s_{1-} + s_{2-})|\uparrow\uparrow\rangle = \hbar(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle),
\end{aligned}$$

and thus

$$|1/2, 1/2; 1, 0\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\Big). \tag{163}$$

Continuing with S_- (or in this case using the fact that we have the lowest nondegenerate M-state) we find

$$|1/2, 1/2; 1, -1\rangle = |\downarrow\downarrow\rangle. \tag{164}$$

3. The state with $M = 0$ is twofold degenerate. One combination is already found in the above procedure. The other is made up of the same two states appearing on the right hand side in Eq. 163. Up to a phase, it is found by requiring it to be orthogonal to the state $|1/2, 1/2; 1, 0\rangle$ or by requiring that $S_+ = s_{1+} + s_{2+}$ gives zero. The result is

$$|1/2, 1/2; 0, 0\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\Big). \tag{165}$$

The convention for the phase is that the higher m_1-value appears with a positive sign.

It is easy to summarize the results in a table, where one puts the states $|j_1, m_1\rangle \otimes |j_2, m_2\rangle$ in the different rows and the states $|j_1, j_2; J, M\rangle$ in the different columns, i.e.

$j_1 \times j_2$	$\vdots$ J $\vdots$
	$\vdots$ M $\vdots$
$\cdots$ $\cdots$	
m_1 m_2	
$\cdots$ $\cdots$	

For the above case we have

$1/2 \times 1/2$		1	1	0	1
		1	0	0	-1
$+1/2$	$+1/2$	1			
$+1/2$	$-1/2$		$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$	
$-1/2$	$+1/2$		$\sqrt{\frac{1}{2}}$	$-\sqrt{\frac{1}{2}}$	
$-1/2$	$-1/2$				1

Note that the recoupling matrix is block-diagonal because of the constraint $M = m_1 + m_2$. The coefficients appearing in the matrix are the socalled Clebsch-Gordan coefficients. We thus have

$$|j_1, j_2; J, M\rangle = \sum_{m_1, m_2} C(j_1, m_1, j_2, m_2; J, M)\, |j_1, m_1\rangle \otimes |j_2, m_2\rangle. \tag{166}$$

Represented as a matrix as done above, it is unitary (because both sets of states are normed). Since the Clebsch-Gordan coefficients are choosen real, the inverse is just the transposed matrix, or

$$|j_1, m_2\rangle \otimes |j_2, m_2\rangle = \sum_{J, M} C(j_1, m_1, j_2, m_2; J, M)\, |j_1, j_2; J, M\rangle. \tag{167}$$

In some cases (like combining two spin 1/2 states) one can make use of symmetry arguments. If a particular state has a well-defined symmetry under permutation of states 1 and 2, then all M-states belonging to a particular J-value have the same symmetry (because $j_{1\pm} + j_{2\pm}$ does not alter the symmetry. This could have been used for the $1/2 \times 1/2$ case, as the highest total M is symmetric, all $S = 1$ states are symmetric. This is in this case sufficient to get the state in Eq. 163.

We will give two other examples. The first is

$1 \times 1/2$		3/2	3/2	1/2	3/2	1/2	3/2
		+3/2	+1/2	+1/2	−1/2	−1/2	−3/2
$+1$	$+1/2$	1					
$+1$	$-1/2$		$\sqrt{\frac{1}{3}}$	$\sqrt{\frac{2}{3}}$			
0	$+1/2$		$\sqrt{\frac{2}{3}}$	$-\sqrt{\frac{1}{3}}$			
0	$-1/2$				$\sqrt{\frac{2}{3}}$	$\sqrt{\frac{1}{3}}$	
-1	$+1/2$				$\sqrt{\frac{1}{3}}$	$-\sqrt{\frac{2}{3}}$	
-1	$-1/2$						1

for instance needed to obtain the explicit states for an electron with spin in an (2p)-orbit coupled to a total angular momentum $j = 3/2$ *(indicated as* $2p_{3/2}$*) with* $m = 1/2$ *is*

$$\phi(\boldsymbol{r}, t) = \frac{u_{2p}(r)}{r} \left(\sqrt{\frac{1}{3}}\, Y_1^1(\theta,\phi)\,\chi_\downarrow + \sqrt{\frac{2}{3}}\, Y_1^0(\theta,\phi)\,\chi_\uparrow \right).$$

The second is

1×1		2	2	1	2	1	0	2	1	2
		$+2$	$+1$	$+1$	0	0	0	-1	-1	-2
$+1$	$+1$	1								
$+1$	0		$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$						
0	$+1$		$\sqrt{\frac{1}{2}}$	$-\sqrt{\frac{1}{2}}$						
$+1$	-1				$\sqrt{\frac{1}{6}}$	$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{3}}$			
0	0				$\sqrt{\frac{2}{3}}$	0	$-\sqrt{\frac{1}{3}}$			
$+1$	-1				$\sqrt{\frac{1}{6}}$	$-\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{3}}$			
0	-1							$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$	
-1	0							$\sqrt{\frac{1}{2}}$	$-\sqrt{\frac{1}{2}}$	
-1	-1									1

This example, useful in the combination of two spin 1 particles or two electrons in p-waves, illustrates the symmetry of the resulting wave functions.

18.3 An example: the Helium atom

As a first-order description of the helium atom, one can consider the independent-electron approximation, starting with a hamiltonian in which the electron-electron interaction is neglected, as well as any interactions involving the spin of the electrons. In that case one has a separable hamiltonian and for each of the electrons the solutions are given by hydrogen-like states ($Z = 2$), characterized by ($n\ell$). Let us investigate the possible ground-state configurations, $(1s)^2$ and the first excited levels $(1s)(2p)$ and $(1s)(2s)$.

- The ground state configurations $(1s)^2$.
  Knowing the two angular momenta involved is sufficient to know the parity of these states, $\Pi = (-)^{\ell_1}(-)^{\ell_2} = +$. The angular momentum recoupling works in the following way.
  - Combining $\ell_1 = 0$ and $\ell_2 = 0$, the only possibility is $L = 0$. The orbital wave function then is symmetric under the interchange of the two electrons 1 and 2.
  - Combining the spins $s_1 = 1/2$ and $s_2 = 1/2$ gives two possibilities, $S = 0$ or $S = 1$. The first possibility is antisymmetric under the interchange of the electrons, the second is symmetric.
  - The total wave function (product of orbital and spin parts) must be antisymmetric for fermions according to the Pauli principle, hence $L = 0$ can only be combined with $S = 0$. This leaves only one possibility for the total angular momentum, $J = 0$. The notation for the only allowed ground state configuration is

    $$(n_1\,\ell_1)(n_2\,\ell_2)\ {}^{2S+1}L_{J^\Pi} = (1s)^2\ {}^1S_{0^+}.$$

- The configurations $(1s)(2p)$ with parity $\Pi = -$.
  - We have $L = 1$, but appearing twice. We can construct the symmetric and antisymmetric combinations,

    $$\phi^{s/a}_{LM_L} = \frac{1}{\sqrt{2}}\left[\frac{u_{1s}(r_1)}{r_1}\,Y_0^0(\Omega_1)\,\frac{u_{2p}(r_2)}{r_2}\,Y_1^{M_L}(\Omega_2) \pm \frac{u_{2p}(r_1)}{r_1}\,Y_1^{M_L}(\Omega_1)\frac{u_{1s}(r_2)}{r_2}\,Y_0^0(\Omega_2)\right]$$

    for the spatial part.
  - The combination of the spins gives again an antisymmetric $S = 0$ and a symmetric $S = 1$ wave function.

  - The allowed configurations are thus obtained by the appropriate antisymmetric combinations of orbital and spin parts,

$$(1s)(2p)\ ^1P_{1^-} \qquad \text{and} \qquad (1s)(2p)\ ^3P_{0^-,1^-,2^-}\,.$$

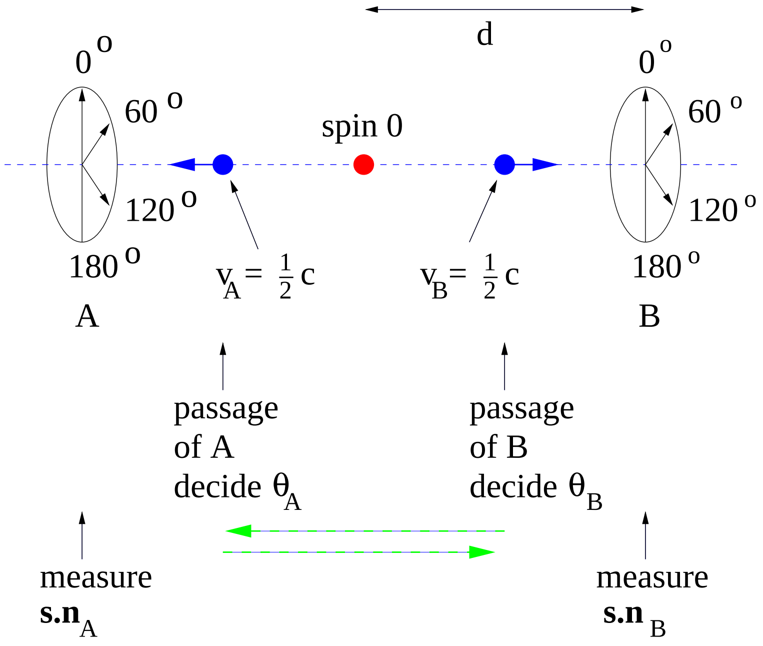
- The configurations $(1s)(2s)$ with parity $\Pi = +$.
  - We have $L = 0$, but now also appearing twice in a symmetric and antisymmetric combination.
  - As above, antisymmetric $S = 0$ and symmetric $S = 1$.
  - This gives the allowed configurations

$$(1s)(2s)\ ^1S_{0^+} \qquad \text{and} \qquad (1s)(2s)\ ^3S_{1^+}\,.$$

19 The EPR experiment

19.1 The 'experiment'

One of the best ways to illustrate the 'absurdness' of quantum mechanics when one tries to understand it with classical means is the EPR experiment, proposed by Einstein, Podolsky and Rosen (1935) to show that quantum mechanics should be wrong. A simplified version of the experiment is the decay of a spin 0 system into two spin 1/2 particles with opposite spin. The spin is measured along a direction perpendicular to the motion of the two particles, which are moving apart at (say) half of the speed of light. The angles θ_A and θ_B, along which the spin is measured can be varied, but the actual decision which angles are measured is only taken (at random) when the particles are halfway[4].



The results of the measurements (which in recent years have actually been performed with a variety of particles over macroscopic distances) are as follows:

- Considering only the measurement at A, the probability to measure a spin along $\hat{\boldsymbol{n}}_A$ is $P(\theta_A, +) = 1/2$ and the probability to measure a spin opposite to this is $P(\theta_A, -) = 1/2$. Similarly at B.
- Given a '+'-measurement at A at a given angle θ_A, the following results are found:

$\|\theta_A - \theta_B\| =$	0°	60°	120°	180°
$P(\theta_A, +; \theta_B, +)$	0	1/4	3/4	1
$P(\theta_A, +; \theta_B, -)$	1	3/4	1/4	0

19.2 A classical explanation?

In any 'realistic' theory the information on the potential measurements for particle A should be a property of particle A and hence stored in the particle. Thus to simplify things, only concentrate on three angles (0°, 60° and 120°). Any event has particles A and B flying apart with known prescriptions for what to do if they encounters a Stern-Gerlach apparatus under a given angle θ_A. E.g.

Event 1: memory_A = $(+ - +)$ memory_B = $(- + -)$
Event 2: memory_A = $(+ + -)$ memory_B = $(- - +)$

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[4] In this way information on the setting of B cannot reach A at the time of measurement

etc. For instance in the first example the prescription tells A that if $\theta_A = 0°$, then a spin measurement yields $+\hbar/2$, if $\theta_A = 60°$, then a spin measurement yields $-\hbar/2$, while if $\theta_A = 120°$, then a spin measurement yields $+\hbar/2$. In each of the events the common origin of A and B is reflected in the complementary prescriptions. This is the only way the first and last colums of the 'experiment' can be explained. Let's now concentrate on the correlations and write some explicit probabilities $P(\theta_A, +; \theta_B, +)$ in terms of the fractions of events with particular memories. We have e.g.

$$\begin{aligned} P(0°, +; 120°, +) &= \sum_{\sigma=-\tau} f(+\sigma-; -\tau+) \\ &= f(++-;--+) \ + \ f(+--;-++) \end{aligned} \tag{168}$$

$$P(60°, +; 120°, +) = f(++-;--+) \ + \ \underbrace{f(-+-;+-+)}_{\geq 0} \tag{169}$$

$$P(0°, +; 60°, +) = \underbrace{f(+-+;-+-)}_{\geq 0} + f(+--;-++), \tag{170}$$

and hence we must have in a realistic theory

$$P(60°, +; 120°, +) + P(0°, +; 60°, +) \geq P(0°, +; 120°, +), \tag{171}$$

which is an explicit example of a Bell inequality. But clearly our 'experiment' above violates this inequality! Thus a realistic theory cannot explain the results in the EPR experiment.

19.3 The quantum-mechanical explanation!

Quantum mechanics can explain the results. Using e.g. the spin states defined with respect to the $\theta = 0$ directions, we know that the AB system is in an antisymmetric (spin zero) state,

$$|AB\rangle = \frac{1}{\sqrt{2}} \left(|A\uparrow\rangle \otimes |B\downarrow\rangle - |A\downarrow\rangle \otimes |B\uparrow\rangle \right) \tag{172}$$

Using the rotated spin states along an arbitrary direction $\hat{\boldsymbol{n}}$, it is straightforward to check the results of the EPR experiment. Given a '+'-measurement at A, the wave function becomes

$$|A\uparrow\rangle \otimes |B\downarrow\rangle$$

and the probability

$$P(0°, +; \theta_B, +) = \left| \langle A\uparrow||A\uparrow\rangle \, \langle \theta_B, +||B\downarrow\rangle \right|^2 = \sin^2(\theta_B/2). \tag{173}$$

For any other angle for θ_A, simply choose this as the quantization axis, to see that the result only depends on $\theta_A - \theta_B$.

A Translations (English → Dutch)

observable	=	observabele
momentum	=	impuls (hoeveelheid van beweging)
angular momentum	=	impulsmoment
measuring device	=	meetapparaat
wave function	=	golffunctie
state	=	toestand
probability	=	waarschijnlijkheid
square integrable	=	kwadratisch integreerbaar
plane wave	=	vlakke golf
Hilbert space	=	Hilbertruimte
expectation value	=	verwachtingswaarde
hermitean	=	hermitisch
self-adjoint	=	zelf-geconjugeerd
diagonal	=	diagonaal
transition	=	overgang
standard deviation	=	standaard afwijking
eigenvalue	=	eigenwaarde
eigenfunction	=	eigenfunctie
eigenstate	=	eigentoestand
degenerate	=	ontaard
complete	=	volledig
Hamiltonian	=	Hamiltoniaan
stationary state	=	stationaire toestand