Quantum Mechanics

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Voorwoord

Het college Quantummechanica wordt dit najaar verzorgd door Prof. Piet Mulders geassisteerd door Drs. Jorn Boomsma bij het werkcollege.

Het college volgt in grote lijnen het boek *Quantum Mechanics* van F. Mandl (Cambridge University Press). De aantekeningen geven soms een iets andere kijk op de stof, maar bevatten in essentie geen stof die niet ook in het boek te vinden is. In een appendix worden een aantal essentiële vaardigheden gegeven, die de student in de meeste gevallen al in een ander college gezien zal hebben.

Het gehele vak beslaat 8 studiepunten en wordt gegeven in periodes 2, 3 en 4. Wekelijks worden 2 uur hoorcollege gegeven, 1 uur wordt besteed aan een presentatie van een van de studenten en vragen, terwijl er 2 uur werkcollege zijn. Daarnaast moeten er opgaven worden ingeleverd, die worden beoordeeld. Na blok 3 wordt een deeltentamen afgenomen (schriftelijk). De opgaven en het deeltentamen vormen onderdeel van de toetsing. Het geheel wordt afgesloten met een (mondeling) tentamen. Dit tentamen, waarbij boek en uitgewerkte opgaven geraadpleegd mogen worden, gaat behalve over theoretische aspecten (afleidingen niet van buiten leren!) ook over opgaven die tijdens het werkcollege zijn behandeld. De hierboven genoemde regeling geldt voor studenten die actief deelnemen aan colleges en werkcolleges.

Piet Mulders
Oktober 2008

Schedule (indicative)

	Material in book	Material in notes
Week 44	1.1, 1.2	1
Week 45	1.3, 1.4	2
Week 46	2.1, 2.2	3
Week 47	2.3, 2.4	4
Week 48	2.5	5
Week 49	2.6, 2.7	6, 7
Week 50	12.1-4	8, 9
Week 2	3.1, 3.2, 3.3	10, 11
Week 3	4.1, 4.2	12, 13
Week 4	4.3, 4.4	14, 15
Week 6	5.1, 5.2, 5.3, 5.8	16, 17
Week 7	5.4, 5.5, 5.6, 6.1, 6.3*	17, 18
Week 8	7.1, 7.2, 7.3, 7.4	19, 20
Week 9	7.5	21
Week 10	8.1, 8.2, 8.3	22
Week 11	9.1, 9.2, 9.3, 9.4, 9.5*	23, 24
Week 12	10.1, 10.2, 10.3	25, 26

Literature

1. F. Mandl, *Quantum Mechanics*, Wiley 1992
2. D.J. Griffiths, *Introduction to Quantum Mechanics*, Pearson 2005
3. C. Cohen-Tannoudji, B. Diu and F. Laloë, *Quantum Mechanics I and II*, Wiley 1977
4. J.J. Sakurai, *Modern Quantum Mechanics*, Addison-Wesley 1991
5. E. Merzbacher, *Quantum Mechanics*, Wiley 1998
6. B. Bransden and C. Joachain, *Quantum Mechanics*, Prentice hall 2000

Contents

1 Observables and states

For the description of an event or an object, to which we will refer as a physical system, we use observations and physical quantities. 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. Classically *the state of an electron* can be specified by a (minimal set of) measurable quantities, for instance $\{\boldsymbol{r}(t), \boldsymbol{p}(t), \boldsymbol{s}, \ldots\}$, where $\boldsymbol{s}$ denotes the intrinsic angular momentum (spin) and in the ... things like charge and mass can be specified.

The above is no longer true in quantum mechanics. In particular for an electron in an atom the above classical description in which the observables are tied to the electron as a series of numbers it is carrying around becomes more subtle. In the quantum mechanical description the observables are not tied to the system, but they refer to an appropriate measuring device or production mechanism. Mathematically, such devices are described by *operators*. The physical system is then described by a *wave function*, that is *not* observable!

Nevertheless, the notion that an electron is at a position $\boldsymbol{r}_1$ at time t_1 and at a position $\boldsymbol{r}_2$ at time t_2 makes sense. This is e.g. the case in the well-known two-slit experiment, if we produce an electron at position $\boldsymbol{r}_1$ (the source) at time t_1 and detect it at position $\boldsymbol{r}_2$ (the screen) at time t_2. Such states are specified by $|\boldsymbol{r}_1, t_1\rangle$ and $|\boldsymbol{r}_2, t_2\rangle$. While classically an electron will follow *one* path from $\boldsymbol{r}_1(t_1)$ to $\boldsymbol{r}_2(t_2)$, determined by the equations of motion, there is not such a thing as a unique path in quantum mechanics. Feynman has shown that one can formulate the outcome of a quantum mechanical measurement (probability to go from point 1 to 2) in terms of a weighted superposition of paths, of which the classical path is the most probable one. The amazing thing of quantum mechanics is that even for *one* electron more paths are possible. The path integral formulation of quantum mechanics will be discussed in advanced treatments.

The weight of the possible paths are determined by the action, a concept which may have been discussed in the context of classical mechanics. The path for which the action is minimal is the classical path. Other paths for which the deviations of the action are smaller or of the order of Planck's constant, however, still contribute. This also determines the domain where quantum mechanics is needed to get a good description of nature, namely that where the action itself is of the order of *Planck's constant*,

$$h = 6.626 \times 10^{-34} \text{ J s}.$$

The action along a path (and the unit of h) corresponds to energy × time and/or to momentum × distance. Often it turns out to be convenient to use the *reduced Planck's constant* $\hbar = h/2\pi = 1.055 \times 10^{-34}$ J s $=$ 6.582×10^{-16} eV s in equations.

1.1 States ↔ wave functions

As stated already, the state of a system is specified by the wave function. Denoting the state of a system as $|\psi\rangle$, it in general does not correspond to a fixed position. Rather, it is determined by a complex function depending on the position and the time,

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

which contains *all* information on the system. This is one of the basic assumptions of quantum mechanics. For instance its modulus squared gives the probability per volume, or precisely

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

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 spreading of the wave function corresponds to the fact that in quantum mechanics paths are not unique. For an electron being in a state $|\boldsymbol{r}_1, t_1\rangle$ the wave function would for $t = t_1$ be a sharp peak around $\boldsymbol{r}_1$, but with time progressing the wave function will spread. At time $t = t_2$ there is a probability (less than one) to find the electron at $\boldsymbol{r}_2$. But when finding the electron there, we have a new starting point. The state collapses into $|\boldsymbol{r}_2, t_2\rangle$.

The states or the wave functions describing a system form a linear space, called a *Hilbert space* $\mathscr{H}$. The Hilbert space of wave functions is that of square integrable functions, denoted $\mathscr{H} = L^2(R^3)$.

> *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 see how we can work with these states without problems.*

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

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

is a possible state of the system, $\psi \in \mathscr{H}$. This is what linear space means. But note that for the linear combination the probability

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

is 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 the 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 modulus 1) has no consequences. for the probabilities!*

It is the function ψ that determines the state of a system, one talks about "the state ψ" which is denoted by $|\psi\rangle$ and is referred to as a *ket*. The ket-notation is useful in many manipulations.

One of these manipulations is the definition of a scalar product defined in the Hilbert space of (ket) states,

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

This socalled *bracket* satisfies $\langle\psi_1|\psi_2\rangle = \langle\psi_2|\psi_1\rangle^*$. The object $\langle\psi|$ is called a *bra.* Two states for which the scalar product gives zero are called *orthogonal.* With the scalar product we can write Eq. 2 as $\langle\psi|\psi\rangle = 1$. Another relation, that we will encounter later is that the value of the wave function is the scalar product of states $|\psi\rangle$ and $|\boldsymbol{r},t\rangle$,

$$\psi(\boldsymbol{r},t) = \langle\boldsymbol{r},t|\psi\rangle. \tag{5}$$

An important feature of linear spaces is that one can construct a basis of states. The scalar product, moreover, makes it possible to choose an orthonormal basis. This is in particular convenient when the space is small, for instance two-dimensional. An example of this could be an electron trapped in a fixed position with two spin orientations (or what is in a laboratory nowadays easier an atom with two spin possibilities). Then one can describe the system in terms of two basis states $|\uparrow\rangle$ and $|\downarrow\rangle$. If these two states are orthogonal (as in general spin states are, something we will see later) and normalized we may use them as basis states,

$$|\uparrow\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |\downarrow\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \tag{6}$$

and it is possible to denote a general spin state as a superposition of these two, thus as a 2-component (complex) vector,

$$|1\rangle = a_1|\uparrow\rangle + a_2|\downarrow\rangle = \chi_1 = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}.$$

In this two-dimensional spinor space one can add any two spinors and multiply them with complex numbers,

$$c_1\chi_1 + c_2\chi_2 = c_1 \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} + c_2 \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} c_1\, a_1 + c_2\, b_1 \\ c_1\, a_2 + c_2\, b_2 \end{pmatrix}, \tag{7}$$

to get another spinor and one can define a scalar product of two spinors,

$$\langle 1|2\rangle = \chi_1^\dagger \chi_2 = \begin{pmatrix} a_1^* & a_2^* \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = a_1^* b_1 + a_2^* b_2, \tag{8}$$

in which the bra $\langle 1|$ is the (adjoint) row vector $\chi_1^\dagger \equiv (a_1^*\ a_2^*)$. It is trivial to check that the basis states in Eq. 6 are indeed orthonormal.

1.2 Observables ↔ operators

What about the observables. Given a system (e.g. an atom) we want to know some things, the position, the momentum or angular momentum. In quantum mechanics these observables are no longer numbers that are uniquely tied to the system. 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:

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

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

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

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

$$\hat{\boldsymbol{r}}\psi(\boldsymbol{r},t) \equiv \boldsymbol{r}\psi(\boldsymbol{r},t), \tag{10}$$

$$\hat{\boldsymbol{p}}\psi(\boldsymbol{r},t) \equiv -i\hbar\boldsymbol{\nabla}\psi(\boldsymbol{r},t). \tag{11}$$

> *Actually $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{p}}$ each 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 $\mathscr{H}$ of which the value in a particular point $\boldsymbol{r}$ is given by $x\,\psi(\boldsymbol{r})$,*
>
> $$\hat{x}\psi(x,y,z,t) = x\,\psi(x,y,z,t).$$

When our states are denoted as n-component spinors the operators are (of course) $n \times n$ matrices.

---

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

Expectation values and hermitean operators

However, the action of an operator, such as the position operator, does not give us the position of the system. The fundamental connection between the observable properties of a system and its state is given by the following basic property of quantum mechanics (one of the postulates):

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,

$$\langle A\rangle_\psi = \langle\psi|\hat{A}|\psi\rangle = \langle\psi|\hat{A}\,\psi\rangle = \int d^3\boldsymbol{r}\;\psi^*(\boldsymbol{r},t)\,\hat{A}\psi(\boldsymbol{r},t). \tag{12}$$

This expectation value is the average outcome of a (large) number of measurements.

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, thus

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

Expectation values are in fact special examples of what are called the *matrix elements* of $\hat{A}$,

$$\langle\psi_1|\hat{A}|\psi_2\rangle = \langle\psi_1|\hat{A}\psi_2\rangle = \int d^3\boldsymbol{r}\;\psi_1^*(\boldsymbol{r},t)\,\hat{A}\psi_2(\boldsymbol{r},t), \tag{13}$$

namely those where $\psi_1 = \psi_2$. An expectation value $\langle A\rangle_\psi = \langle\psi|\hat{A}|\psi\rangle$ is also 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.* For linear operators we can derive the following property for the matrix elements of a hermitean operator:

Theorem: $= \hat{A}$ is hermitean $\Longleftrightarrow \langle\psi_1|\hat{A}|\psi_2\rangle = \langle\psi_2|\hat{A}|\psi_1\rangle^* = \langle\hat{A}\psi_1|\psi_2\rangle$

or formulated with functions,

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

> *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*
>
> $$\sum_{m,n=1}^{2} c_m^* c_n \left[\langle\psi_m|\hat{A}|\psi_n\rangle - \langle\psi_n|\hat{A}|\psi_m\rangle^*\right] = 0.$$
>
> *Since c_1 and c_2 are arbitrary complex numbers each term in the sum must be zero.*

Standard deviation

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

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

Note that $\hat{A} - \langle\hat{A}\rangle$ means subtracting a constant from an operator, which more neatly should read $= \hat{A} - \langle\hat{A}\rangle\,\mathbb{I}$. It is straightforward to show that

$$(\Delta A)^2 = \langle(\hat{A} - \langle\hat{A}\rangle)^2\rangle = \langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2, \tag{14}$$

where the subscript ψ on ΔA is omitted, as is usually done if it is clear within the context. 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 $\langle\hat{A}\rangle$ is real - one can rewrite

$$\begin{aligned}(\Delta A)^2 &= \int d^3\boldsymbol{r}\ \psi^*\,(\hat{A}-\langle\hat{A}\rangle)^2\psi \\ &= \int d^3\boldsymbol{r}\ [(\hat{A}-\langle\hat{A}\rangle)\psi]^*\,(\hat{A}-\langle\hat{A}\rangle)\psi = \int d^3\boldsymbol{r}\ |(\hat{A}-\langle\hat{A}\rangle)\psi|^2,\end{aligned} \tag{15}$$

From this result one immediately gets the following theorem

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

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 $\hat{A}$.

1.3 Eigenvalues and eigenstates of hermitean operators

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 equates both lines, 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. One 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,
$\langle\psi_m|\psi_n\rangle = \int d^3\boldsymbol{r}\ \psi_m^*\,\psi_n = \delta_{mn}$.

---

[2] The Kronecker delta symbol is given by $\delta_{mn} = 1$ if $m = n$, while the outcome is zero if $m \neq n$.

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

$$\psi = \sum_n c_n \, \psi_n, \tag{16}$$

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

$$c_n = \langle \psi_n | \psi \rangle = \int d^3\boldsymbol{r} \; \psi_n^* \, \psi. \tag{17}$$

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

$$\sum_n |c_n|^2 = 1. \tag{18}$$

Using the expansion theorem it is straightforward to write

$$\langle A \rangle_\psi = \langle \psi | \hat{A} | \psi \rangle = \sum_n |c_n|^2 \, \langle A \rangle_{\psi_n} = \sum_n |c_n|^2 \, a_n = \overline{a}, \tag{19}$$

$$(\Delta A)^2_\psi = \sum_n |c_n|^2 \, (a_n - \langle A \rangle)^2 = \sum_n |c_n|^2 \, (a_n - \overline{a})^2, \tag{20}$$

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.

Summarizing measurements in quantum mechanics

- Any state ψ can be expressed as a superposition of eigenstates ψ_n of the operator $\hat{A}$, with coefficients c_n (Eq. 16) given by $c_n = \langle \psi_n | \psi \rangle$ (Eq. 17).
- The average outcome of a number of measurement, the expectation value of the operator $\hat{A}$ and its standard deviation are given by Eqs 19 and 20, which leads to the unavoidable interpretation that the outcome of a single measurement is a_n with probability $P(a_n) = |c_n|^2$. This is the central issue in quantum mechanics!
- Thus only the eigenvalues of $\hat{A}$ are observed! The expression for the expectation value (Eq. 19) can be rewritten

  $$\langle A \rangle_\psi = \sum_n |c_n|^2 \, a_n = \sum_n P(a_n) \, a_n, \tag{21}$$

  where the probability to find the state ψ in an eigenstate is given by

  $$P(a_n) = |c_n|^2 = |\langle \psi_n | \psi \rangle|^2. \tag{22}$$

  If there are degenerate eigenvalues we get $P(a_n) = \sum_{r=1}^{s} |c_{nr}|^2$, where c_{nr} with $r = 1, \ldots, s$ are the coefficients of s eigenstates with the same eigenvalue a_n.
- After a 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). This phenomenon is referred to as "collapse of the wave function". Although it seems crazy, it shouldn't worry us as wave functions are not observable!

Appendix: Basic Knowledge

Complex numbers

Complex numbers z with real part and imaginary part and complex conjugate z^*,

$$z = \mathrm{Re}\, z + i\, \mathrm{Im}\, z, \qquad z^* = \mathrm{Re} z - i\, \mathrm{Im} z,$$

absolute value or modulus squared $|z|^2 = zz^*$ and representation in terms of phase angle φ,

$$z = |z|\, e^{i\,\varphi} = |z|(\cos\varphi + i\, \sin\varphi).$$

Linear Algebra

Basic concepts from linear algebra: linear space over the complex numbers, vectors in a linear space, linear independence, inner product, basis, completeness and orthogonality, linear operators. Also representation of operators as matrices and determination of eigenvalues and eigenvectors of the matrices.

Differentiation and integration

Principles of differentiation and integration for functions including those with more than one argument. Chain rule for differentiation. Partial integration,

$$\int_a^b dx\ f(x)\, dg(x) = f(x)\, g(x)\Big|_a^b - \int_a^b dx\ g(x)\, df(x).$$

Change of variables

Change of variables and corresponding Jacobian, including for instance the transition from Cartesian $(x,\ y,\ z)$ to cilindrical coordinates $(\rho,\ \varphi,\ z)$, where $\rho = \sqrt{x^2+y^2}$ or to polar coordinates $(r,\ \theta,\ \varphi)$ with $r = \sqrt{x^2+y^2+z^2}$,

$$\begin{aligned} x &= \rho\, \cos\varphi = r\, \sin\theta\, \cos\varphi, \\ y &= \rho\, \sin\varphi = r\, \sin\theta\, \sin\varphi, \\ z &= r\, \cos\theta, \end{aligned}$$

with as result

$$\begin{aligned} \int d^3r &= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \\ &= \int_0^{\infty} r^2\, dr \int_{-1}^{1} d\cos\theta \int_0^{2\pi} d\varphi\ = \int_0^{\infty} r^2\, dr \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\varphi \\ &= \int_{-\infty}^{\infty} dz \int_0^{\infty} \rho\, d\rho \int_0^{2\pi} d\varphi\ . \end{aligned}$$

Statistics

Basic concepts from statistics, such as mean and standard deviation,

$$\overline{x} = \frac{1}{N}\sum_i x_i, \qquad \Delta x = \sqrt{\frac{\sum_i (x_i - \overline{x})^2}{N}}.$$

Questions

1. Why is there an i and an $\hbar$ in $\hat{p}_x = -i\hbar\frac{d}{dx}$.
2. Give differences between classical mechanics and quantum mechanics in the way a system is characterized and in measuring properties.
3. The outcome of measurements are real numbers. What is the implication for operators in quantum mechanics?
4. What do we learn from the outcome of a single measurement?
5. When is the outcome of a measurement unique?
6. What is the meaning of the expectation value of an operator?
7. Show for a given state ψ that $(\Delta A)^2 = \langle A^2\rangle - \langle A\rangle^2$.

Exercises

Exercise 1.1

Consider the one-dimensional wave Gaussian wave function in the domain $-\infty < x < \infty$,

$$\psi(x,t) = N\, e^{-\lambda(x-a)^2/2}\, e^{-i\omega t},$$

with constants N, a and λ.

(a) Determine N.

(b) Find $\langle x\rangle$, $\langle x^2\rangle$, and Δx.

(c) Sketch the graph of $\rho(x) = |\psi(x)|^2$.

Useful integrals (also for later applications) are

$$\begin{aligned}
\int_0^\infty dx\; e^{-px^2} &= \frac{1}{2}\sqrt{\frac{\pi}{p}},\\
\int_0^\infty dx\; x^{2n}\, e^{-px^2} &= \frac{(2n-1)!!}{2\,(2p)^n}\sqrt{\frac{\pi}{p}} \quad \text{(for } p>0,\; n=1,3,\ldots)\\
\int_0^\infty dx\; x^{2n+1}\, e^{-px^2} &= \frac{n!}{2\,p^{n+1}} \quad \text{(for } p>0,\; n=0,1,\ldots).
\end{aligned}$$

Be aware of the domain of integration. Note that $n! = n(n-1)\ldots 1$ (with $0! = 1$), $(2n)!! = 2n(2n-2)\ldots 2$, $(2n-1)!! = (2n-1)(2n-3)\ldots 1$.

Exercise 1.2

At time $t = 0$ a one dimensional system is described by the wave function

$$\phi(x) = \begin{cases} Ax/a & 0 < x < a \\ A(b-x)/(b-a) & a \leq x < b \\ 0 & \text{otherwise,} \end{cases}$$

with A, a and b constants.

(a) Normalize ϕ (i.e. find A in terms of a and b).

(b) Sketch $\phi(x)$ as a function of x.

(c) What is the probability of finding the system to the left of a? Check your result in the limiting cases $b = a$ and $b = 2a$.

(d) What is the expectation value of x?

Exercise 1.3

(a) Show that the spinor

$$|\chi_1\rangle = \begin{pmatrix} \sqrt{\frac{2}{3}} \\ \sqrt{\frac{1}{3}} \end{pmatrix}$$

is normalized

(b) Find a spinor that is orthogonal to the spinor under (a).

Exercise 1.4

Consider the one dimensional wave function in the domain $-\infty < x < \infty$,

$$\psi(x,t) = A\, e^{-\lambda|x|}\, e^{-i\omega t},$$

where A, λ and ω are real, positive constants.

(a) Normalize ψ.

(b) Determine the expectation values of x and x^2.

(c) Find the standard deviation of x. Sketch the graph of $|\psi|^2$, as a function of x, and mark the points $\langle x\rangle + \Delta x$ and $\langle x\rangle - \Delta x$. What is the probability that the particle is found outside this range?

Useful integrals (also for later applications) are

$$\int dx\ e^{-x} = -e^{-x} \qquad \text{and} \qquad \int dx\ x^n\, e^{-x} = -x^n\, e^{-x} + n \int dx\ x^{n-1}\, e^{-x} \quad \text{for } n \geq 1,$$

$$\int_0^\infty dx\ x^n\, e^{-x} = n!$$

Exercise 1.5

Consider the (3-dimensional) spartial wave function of an electron in the groundstate of Hydrogen, $\phi_{000}(\boldsymbol{r}) = N\, e^{-r/a_0}$ (we will discuss the quantum numbers, the subscript '000' and the scale a_0 later).

(a) Show that the normalization is given by $N = 1/\sqrt{\pi\, a_0^3}$.

(b) What is the probability to find the electron at $r < a_0$.

(c) What is the probability to find the electron at $a_0 < r < 2\, a_0$.

(d) Calculate the expectation values of x, r and r^2, x^2.

(e) Calculate the expectation values of $p_x = -i\hbar\, \partial/\partial x$, p_x^2 and $\boldsymbol{p}^2$.

[Hint: Note that $\partial r/\partial x = x/r$.]

Exercise 1.6

Consider the angular momentum operator

$$\ell_z = -i\hbar \left(x\, \frac{\partial}{\partial y} - y\, \frac{\partial}{\partial x} \right).$$

(a) Show that ℓ_z acting on a function depending only on $r = \sqrt{x^2 + y^2 + z^2}$ gives zero.

(b) Show that

$$\psi_\pm^z(\boldsymbol{r}) = N\,(x \pm i\, y)\, f(r)$$

are eigenfunctions of the operator ℓ_z. What are the eigenvalues?

2 Time evolution

2.1 The Hamiltonian

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,

$$i\hbar\frac{\partial\psi}{\partial t} \equiv \hat{H}\psi(\boldsymbol{r},t). \tag{23}$$

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*
>
> $$\frac{1}{-i\hbar}\int d^3\boldsymbol{r}\;\left[(\hat{H}\psi)^*\psi - \psi^*(\hat{H}\psi)\right] = 0, \tag{24}$$
>
> *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,

$$\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m} + V(\hat{\boldsymbol{r}}) = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\boldsymbol{r}). \tag{25}$$

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

$$\hat{H}(\hat{\boldsymbol{r}},\hat{\boldsymbol{p}},\ldots)\phi_n(\boldsymbol{r}) = E_n\phi_n(\boldsymbol{r}). \tag{26}$$

The eigenvalues are called the *energies* E_n. 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.

In that case the full time-dependent solutions of the Schrödinger equation are easily obtained. The Hamiltonian on the RHS of Eq. 23 only affects the spatial dependence, the left hand side doesn't care about spatial dependence. Using completeness we can at any time write

$$\psi(\boldsymbol{r},t) = \sum_n c_n(t)\,\phi_n(\boldsymbol{r}). \tag{27}$$

Inserting this expansion in Eq. 23 we find with the knowledge of Eq. 26 that the coefficients $c_n(t)$ satisfy

$$i\hbar\,\phi_n(\boldsymbol{r})\,\frac{dc_n}{dt} = E_n\,\phi_n(\boldsymbol{r})\,c_n(t) \quad\Longrightarrow\quad i\hbar\,\frac{dc_n}{dt} = E_n\,c_n(t) \tag{28}$$

giving immediately the time-dependent solutions

$$\psi(\boldsymbol{r},t) = \sum_n c_n(0)\,\phi_n(\boldsymbol{r})\,e^{-iE_nt/\hbar} = \sum_n c_n(0)\,\psi_n(\boldsymbol{r},t), \tag{29}$$

with time-dependent solutions

$$\psi_n(\boldsymbol{r},t) = \phi_n(\boldsymbol{r})\,e^{-iE_nt/\hbar}, \tag{30}$$

Each of these ψ_n-solutions is referred to as a *stationary state*.

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

$$-\frac{\hbar^2}{2m}\,\boldsymbol{\nabla}^2\,\phi(\boldsymbol{r}) = E\,\phi(\boldsymbol{r}) \tag{31}$$

are the plane waves

$$\phi_k(\boldsymbol{r}) = \exp(i\boldsymbol{k}\cdot\boldsymbol{r}) \qquad \textit{with} \qquad E(\boldsymbol{k}) = \frac{\hbar^2\boldsymbol{k}^2}{2m}. \tag{32}$$

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

$$\psi_k(\boldsymbol{r},t) = \exp(i\boldsymbol{k}\cdot\boldsymbol{r} - i\omega\,t), \tag{33}$$

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

2.2 Time dependence of expectation values

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 (thus we have a stationary state),

$$\psi_n(\boldsymbol{r},0) = \phi_n(\boldsymbol{r}), \tag{34}$$

$$\psi_n(\boldsymbol{r},t) = \phi_n(\boldsymbol{r})\,e^{-iE_nt/\hbar}. \tag{35}$$

In that case the probability to find the system at a particular place is time-independent,

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

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

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

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 $E_n \equiv \hbar\omega_n$,

$$\psi(\boldsymbol{r},0) = c_1\,\phi_1(\boldsymbol{r}) + c_2\,\phi_2(\boldsymbol{r}), \tag{36}$$

$$\psi(\boldsymbol{r},t) = c_1\,\phi_1(\boldsymbol{r})\,e^{-iE_1t/\hbar} + c_2\,\phi_2(\boldsymbol{r})\,e^{-iE_2t/\hbar}. \tag{37}$$

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

$$\int d^3\boldsymbol{r}\;\phi_1^*(\boldsymbol{r})\,\hat{A}\phi_1(\boldsymbol{r}) = A_{11}, \tag{38}$$

$$\int d^3\boldsymbol{r}\;\phi_2^*(\boldsymbol{r})\,\hat{A}\phi_2(\boldsymbol{r}) = A_{22}, \tag{39}$$

$$\int d^3\boldsymbol{r}\;\phi_1^*(\boldsymbol{r})\,\hat{A}\phi_2(\boldsymbol{r}) = A_{12}, \tag{40}$$

$$\int d^3\boldsymbol{r}\;\phi_2^*(\boldsymbol{r})\,\hat{A}\phi_1(\boldsymbol{r}) = A_{21} = A_{12}^*, \tag{41}$$

one obtains

$$\begin{aligned}\langle A\rangle(t) &= \int d^3\boldsymbol{r}\ \psi^*(\boldsymbol{r},t)\hat{A}\psi(\boldsymbol{r},t) \\ &= |c_1|^2\,A_{11} + |c_2|^2\,A_{22} + 2\,\mathscr{R}e\left[c_1^* c_2\,A_{12}\,e^{i(\omega_1-\omega_2)t}\right].\end{aligned} \tag{42}$$

One sees the occurrence of oscillations with a frequency

$$\omega_{osc} = \omega_1 - \omega_2 = \frac{E_1 - E_2}{\hbar}. \tag{43}$$

2.3 Probability and current

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

$$\rho(\boldsymbol{r},t) = |\psi(\boldsymbol{r},t)|^2. \tag{44}$$

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,

$$\frac{\partial}{\partial t}\,\rho + \boldsymbol{\nabla}\cdot\boldsymbol{j} = 0, \tag{45}$$

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

$$-\frac{d}{dt}\int_V d^3\boldsymbol{r}\ \rho(\boldsymbol{r},t) = \int_V d^3\boldsymbol{r}\ \boldsymbol{\nabla}\cdot\boldsymbol{j}(\boldsymbol{r},t) = \int_S d^2\boldsymbol{s}\cdot\boldsymbol{j}(\boldsymbol{r},t), \tag{46}$$

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. 24) one finds that for a commonly used hamiltonian like the one in Eq. 25 the current is given by

$$\boldsymbol{j}(\boldsymbol{r},t) = \frac{i\hbar}{2m}\left[(\boldsymbol{\nabla}\psi)^*\psi - \psi^*(\boldsymbol{\nabla}\psi)\right]. \tag{47}$$

Note that in one dimension the current is given by

$$j(x,t) = \frac{i\hbar}{2m}\left[\left(\frac{d\psi}{dx}\right)^*\psi - \psi^*\left(\frac{d\psi}{dx}\right)\right]. \tag{48}$$

2.4 Multi-particle systems

For more than one particle (or more general a system with more degrees of freedom) the state 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 now is a function in a configuration space $R^3 \otimes R^3 \otimes \ldots$. The probability to find the system is given by

$$P(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N,t)\ d^3\boldsymbol{r}_1\ldots d^3\boldsymbol{r}_N = |\psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N,t)|^2\ d^3\boldsymbol{r}_1\ldots d^3\boldsymbol{r}_N. \tag{49}$$

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,

$$\hat{H} = i\hbar \frac{\partial}{\partial t}, \tag{50}$$

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

$$\hat{H} = H(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{p}}_1, \hat{\boldsymbol{r}}_2, \hat{\boldsymbol{p}}_2, \ldots). \tag{51}$$

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

$$H(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{p}}_1, \hat{\boldsymbol{r}}_2, \hat{\boldsymbol{p}}_2) = H_1(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{p}}_1) + H_2(\hat{\boldsymbol{r}}_2, \hat{\boldsymbol{p}}_2). \tag{52}$$

It is trivial to proof the following theorem.

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

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

then the eigenstates and eigenvalues in $\hat{H}\,\phi = E\,\phi$ are given by

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

But although simple to deal with this is of course not a very interesting case. Usually we have interactions involving potentials that involve the coordinates of many of the particles, e.g. an atom with many electrons.

2.5 Center of mass and relative coordinates for two particles

In the case of two particles one frequently encounters the situation that the potential depends on the distance between the particles,

$$\hat{H} = \frac{\hat{\boldsymbol{p}_1}^2}{2m_1} + \frac{\hat{\boldsymbol{p}_2}^2}{2m_2} + V(\hat{\boldsymbol{r}_1} - \hat{\boldsymbol{r}_2}) = -\frac{\hbar^2}{2m_1}\,\boldsymbol{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\,\boldsymbol{\nabla}_2^2 + V(\boldsymbol{r}_1 - \boldsymbol{r}_2). \tag{53}$$

This hamiltonian is non-separable, but with a little but of work it can be made separable. After changing to center of mass and relative coordinates,

$$\boldsymbol{R} \equiv \frac{m_1}{M}\,\boldsymbol{r}_1 + \frac{m_2}{M}\,\boldsymbol{r}_2, \tag{54}$$

$$\boldsymbol{r} \equiv \boldsymbol{r}_1 - \boldsymbol{r}_2, \tag{55}$$

where $M = m_1 + m_2$, it is easy to proof that

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2M}\,\boldsymbol{\nabla}_R^2}_{H_{CM}} \underbrace{-\frac{\hbar^2}{2\mu}\,\boldsymbol{\nabla}_r^2 + V(\boldsymbol{r})}_{H_{rel}}, \tag{56}$$

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

$$\hat{\boldsymbol{P}} \equiv -i\hbar\,\boldsymbol{\nabla}_R = -i\hbar\,(\boldsymbol{\nabla}_1 + \boldsymbol{\nabla}_2) = \hat{\boldsymbol{p}}_1 + \hat{\boldsymbol{p}}_2, \tag{57}$$

$$\hat{\boldsymbol{p}} \equiv -i\hbar\,\boldsymbol{\nabla}_r = -i\hbar\left(\frac{m_2}{M}\boldsymbol{\nabla}_1 - \frac{m_1}{M}\,\boldsymbol{\nabla}_2\right) = \frac{m_2}{M}\,\hat{\boldsymbol{p}}_1 - \frac{m_1}{M}\,\hat{\boldsymbol{p}}_2, \tag{58}$$

a relation that is identical to the classical one.

Appendix: Basic Knowledge

Gradient of functions

$$\boldsymbol{\nabla} f = \left(\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, \frac{\partial f}{\partial z}\right),$$

with for example $\boldsymbol{\nabla}(\boldsymbol{a}\cdot\boldsymbol{r}) = \boldsymbol{a}$ and using $\partial r/\partial x = x/r$, etc. the result

$$\boldsymbol{\nabla} r = \boldsymbol{r}/r = \hat{\boldsymbol{r}} \quad \text{and} \quad \boldsymbol{\nabla} f(r) = f'(r)\,\hat{\boldsymbol{r}}.$$

Basic differential equations

Examples are differential equations of the form

$$f'(x) = a\,f(x) \quad \Longrightarrow \quad f(x) = C\,e^{a\,x}.$$

Elementary vector calculus

Inner and outer product of vectors and divergence and curl of vector field

$$\boldsymbol{\nabla}\cdot\boldsymbol{V} = \frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z}$$

$$\boldsymbol{\nabla}\times\boldsymbol{V} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ V_x & V_y & V_z \end{vmatrix} = \left(\frac{\partial V_z}{\partial y} - \frac{\partial V_y}{\partial z}, \frac{\partial V_x}{\partial z} - \frac{\partial V_z}{\partial x}, \frac{\partial V_y}{\partial x} - \frac{\partial V_x}{\partial y}\right),$$

with as specific examples $\boldsymbol{\nabla}\cdot\boldsymbol{r} = 3$ and $\boldsymbol{\nabla}\cdot\hat{\boldsymbol{r}} = 2/r$.
Stokes equation states

$$\int_{\text{volume}} d^3r\ \boldsymbol{\nabla}\cdot\boldsymbol{V}(\boldsymbol{r}) = \int_{\text{surface}} d^2s\cdot\boldsymbol{V}(\boldsymbol{r}).$$

Questions

1. Which operator describes the time dependence of states in quantum mechanics?
2. What are stationary states?
3. Give the time dependence of stationary states.
4. What is the time dependence of the expectation value of a (time independent) operator for stationary states?
5. Which phenomenon occurs when an initial states is not a stationary state? What oscillates? What is the frequency of oscillations?
6. Which are the solutions of the Schrödinger equation for a free particle? What is the spatial behavior, what is the time dependence? What is the wave length, what is the frequency?

Exercises

Exercise 2.1

We investigate the situation in which we have two eigenstates ϕ_1 and ϕ_2 of the Hamiltonian with energies E_1 and E_2 and $\tau \equiv h/(E_1 - E_2)$. The expectation values of A are given by $A_{11} = a$, $A_{22} = -a$ and $A_{12} = a\sqrt{3}$. Give $\psi(\boldsymbol{r}, t)$ and determine (plot) the time dependence of $\langle A \rangle(t)$ for the case that at $t = 0$

(a) $\psi(\boldsymbol{r}, 0) = \phi_1(\boldsymbol{r})$.

(b) Same for $\psi(\boldsymbol{r}, 0) = \frac{1}{2}\sqrt{3}\,\phi_1(\boldsymbol{r}) + \frac{1}{2}\phi_2(\boldsymbol{r})$.

(c) Under (a) and (b) the expectation value of A is considered as a function of time. What are (assuming no other states than ϕ_1 and ϕ_2 to be relevant) the possible outcomes and corresponding probabilities of a measurement at time $t = 0$.

Exercise 2.2

A quite common situation in physics is the appearance of two degenerate configurations with the same energy (e.g. two mirror molecules), for which there is an interaction term in the hamiltonian that couples these two configurations. Labeling these two states as $|1\rangle$ and $|2\rangle$ one then has $\langle 1|H|1\rangle = \langle 2|H|2\rangle = E_0$, while $\langle 1|H|2\rangle = \langle 2|H|1\rangle = E_1$ (taken real). Assume the states $|1\rangle$ and $|2\rangle$ to be orthonormal.

(a) Denote the states as two-component spinors, write H as a 2×2 matrix.

(b) Determine the eigenvalues of the hamiltonian, give the eigenstates $|\phi_+\rangle$ and $|\phi_-\rangle$

(c) Give the most general time-dependent solution $|\psi(t)\rangle$.

(d) Given that $|\psi(0)\rangle = |1\rangle$, calculate the time t for which $|\psi(t)\rangle = |2\rangle$.

Exercise 2.3

Calculate the density and the flux for

(a) a plane wave $\phi(x) = A\, e^{\pm ikx}$ in one dimension;

(b) a plane wave, $\phi(\boldsymbol{r}) = A\, \exp(i\,\boldsymbol{k} \cdot \boldsymbol{r})$ in three dimensions;

(c) a wave function of the kind $\phi(\boldsymbol{r}) = (x + i\,y)\, f(r)$ (take $f(r)$ real).

Exercise 2.4

Given the Hamiltonian

$$H = \boldsymbol{\alpha} \cdot \boldsymbol{p} c + mc^2 \;=\; -i\hbar c\, \boldsymbol{\alpha} \cdot \boldsymbol{\nabla} + mc^2.$$

in which $\boldsymbol{\alpha}$ is a constant vector. Derive from the Schrödinger equation and the continuity equation what is the current belonging to the density $\rho = \psi^* \psi$.

Exercise 2.5

Consider in one dimension the coordinate transformation

$$\begin{aligned}
&X \equiv \frac{m_1}{M}\,x_1 + \frac{m_2}{M}\,x_2,\\
&x \equiv x_1 - x_2.
\end{aligned}$$

Show that

$$\begin{aligned}
&\frac{d}{dX} = \frac{d}{dx_1} + \frac{d}{dx_2},\\
&\frac{d}{dx} = \frac{m_2}{M}\,\frac{d}{dx_1} - \frac{m_1}{M}\,\frac{d}{dx_2},
\end{aligned}$$

and derive from this Equation 56.

3 One dimensional Schrödinger equation

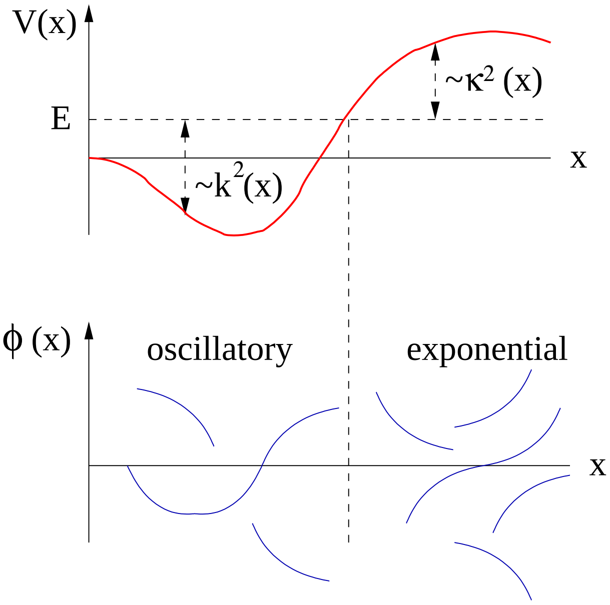
3.1 Spectrum and behavior of solutions

Given the one-dimensional hamiltonian $H = -\hat{p}_x^2/2m + V(\hat{x})$, stationary solutions of the form $\psi(x,t) = \phi(x)\,\exp(-iEt/\hbar)$, are obtained by solving

$$\left[-\frac{\hbar^2}{2m}\,\frac{d^2}{dx^2} + V(x)\right]\,\phi(x) = E\,\phi(x),$$

rewritten as

$$\frac{d^2}{dx^2}\,\phi = -\underbrace{\frac{2m}{\hbar^2}\,(E - V(x))}_{k^2(x)}\,\phi(x). \tag{59}$$



We distinguish two situations:
(i) $k^2(x) \geq 0$ in the region where $E \geq V(x)$. In that case the change of slope is opposite to the sign of the wave function, which implies that the solution always *bends towards the axis*. Looking at the case that $k^2(x) = k^2 = 2m(E - V_0)/\hbar^2$ (constant potential V_0) one has:

$$\phi(x) = A\,\sin kx + B\,\cos kx, \tag{60}$$

or

$$\phi(x) = A'\,e^{i\,kx} + B'\,e^{-i\,kx}. \tag{61}$$

(ii) $k^2(x) = -\kappa^2(x) \leq 0$ in the region where $E \leq V(x)$. In that case the change of slope has the same sign as the wave function, which implies that the solution always *bends away from the axis*. Looking at the case that $k^2(x) = -\kappa^2 = -2m(V_0 - E)/\hbar^2$ (constant potential V_0) one has:

$$\phi(x) = A\,\sinh\kappa x + B\,\cosh\kappa x, \tag{62}$$

or

$$\phi(x) = A'\,e^{\kappa x} + B'\,e^{-\kappa x}. \tag{63}$$

3.2 Boundary conditions and matching conditions

In order to find proper solutions of the Schrödinger equation, which is a second order (linear) differential equation, one needs $d^2\phi/dx^2$, hence $\phi(x)$ and $d\phi/dx$ must be continuous. The second condition implies

$$\left.\frac{d\phi}{dx}\right|_{a+\epsilon} - \left.\frac{d\phi}{dx}\right|_{a-\epsilon} = \int_{a-\epsilon}^{a+\epsilon} dx\; \frac{d^2\phi}{dx^2} = \frac{2m}{\hbar^2}\int_{a-\epsilon}^{a+\epsilon} dx\;\left(V(x)-E\right)\phi(x) = 0$$

Thus continuity not necessarily requires a continuous potential, but it is necessary that the potential remains finite. In points where the potential becomes infinite one must be careful, e.g. by studying it as a limiting case.

Cases in which the potential makes a jump are studied by imposing matching conditions from both sides, namely equating the wave function and its derivative. Because one in quantum mechanics often takes some freedom in the normalization (to be imposed later) or one uses the (non-renormalizable) plane waves, one often chooses to equate the ratio of derivative and wave function, the socalled logarithmic derivative. Thus:

$$\lim_{\epsilon\to 0}\phi(a-\epsilon) = \lim_{\epsilon\to 0}\phi(a+\epsilon) \tag{64}$$

$$\lim_{\epsilon\to 0}\left.\frac{d\phi}{dx}\right|_{a-\epsilon} = \lim_{\epsilon\to 0}\left.\frac{(d\phi}{dx}\right|_{a+\epsilon}, \tag{65}$$

or instead of the latter

$$\lim_{\epsilon\to 0}\left.\frac{(d\phi/dx)}{\phi(x)}\right|_{a-\epsilon} = \lim_{\epsilon\to 0}\left.\frac{(d\phi/dx)}{\phi(x)}\right|_{a+\epsilon}. \tag{66}$$

The behavior at infinity (let's simply assume the potential to be zero) depends on the energy, e.g. if $E = -\hbar^2\kappa^2/2m < 0$ one must have

$$\lim_{x\to\infty}\phi(x) = C\,e^{-\kappa x} \longrightarrow 0, \tag{67}$$

$$\lim_{x\to-\infty}\phi(x) = C\,e^{\kappa x} \longrightarrow 0. \tag{68}$$

If the energy $E = \hbar^2k^2/2m > 0$ one could have in case of an wave from the left with incoming flux $\hbar k/m$ (allowing to be general for a reflected wave) the boundary condition

$$\lim_{x\to-\infty}\phi(x) = e^{i\,kx} + A_R\,e^{-i\,kx}. \tag{69}$$

In a particular physics problem, one might look for a solution with only a transmitted wave

$$\lim_{x\to\infty}\phi(x) = A_T\,e^{i\,kx}. \tag{70}$$

with a transmitted flux $|A_T|^2\,\hbar k/m$ and thus a transmission probability (transmitted/incoming flux) $T = |A_T|^2$. With the above ingredients several one-dimensional problems can be solved. Some examples of potential wells and barriers will be discussed below. In the case of reflection and transmission one will find conservation of probability (fluxes), $T + R = 1$. If the potential for $x \to \infty$ happens to go to a constant value $V(\infty) > E$, the solutions in the region $V(-\infty) < E < V(\infty)$ will for $x \to \infty$ behave like

$$\lim_{x\to\infty}\phi(x) = C\,e^{-\kappa x} \tag{71}$$

with $E - V(\infty) = -\hbar^2\kappa^2/2m$. In that case current conservation requires $R = |A_R|^2 = 1$ and the reflection amplitude can be written as a simple phase. Defining $A_R = -e^{2i\delta}$ we find the asymptotic behavior

$$\lim_{x\to-\infty}\phi(x) = e^{i\,kx} - e^{2i\delta}\,e^{-i\,kx} \;\propto\; \sin(kx-\delta). \tag{72}$$

Given a particular potential we note three domains:
(i) No solutions exist when $E \le V_{\rm min}$. In that case one has everywhere $k^2(x) \le 0$ and there is no way that the exponentially behaving solutions at $\pm\infty$ can be matched without a region where the solution bends back towards the axis, i.e. a region where $E \ge V(x)$.
(ii) In the regin $V_{\rm min} < E < V_{\rm asym}$ (where $V_{\rm asym}$ is the lowest asymptotic value of the potential) one has a discrete energy spectrum corresponding to a discrete set of solutions: starting with a vanishing exponential at, say, $x = -\infty$, one will find in general a solution that at $x = +\infty$ behaves as a linear combination of two exponential functions (as in Eq. 63). Only for very specific energies the coefficient of the growing exponential $e^{\kappa x}$ will be zero and one finds a normalizable solution. These localized solutions, found for discrete energies, are referred to as *bound states*.
(iii) In the region $E \ge V_{\rm asym}$ one has a continuous spectrum of which the solutions at infinity oscillate or equivalently are complex-valued plane waves (with definite momentum). One always can find such a solution. This is even true if the asymptotic values of the potential at $x = \pm\infty$ are not equal.

Finally, considering an infinitely high potential (e.g. for $x > 0$) as the limit of a large potential V_0 for $x > 0$ one must match on to the solution $e^{-\kappa x}$ with $\kappa^2 = 2mV_0/\hbar^2$, leading to

$$\lim_{x\uparrow 0} \frac{(d\phi/dx)}{\phi(x)} = \lim_{V_0\to\infty} \sqrt{\frac{2mV_0}{\hbar^2}} = \infty, \tag{73}$$

which requires $\phi(0) = 0$ and a finite derivative as only nontrivial possibility.

3.3 The infinite square well

We start by considering the potential

$$V(x) = 0 \quad \text{for } |x| < a \qquad \text{and} \qquad V(x) = \infty \quad \text{for } |x| \ge a.$$

As discussed in the previous section, the wave function is zero for $|x| > a$. For $E \le 0$ one would have solutions of the form

$$\phi(x) = A\,e^{\kappa x} + B\,e^{-\kappa x},$$

with $\kappa^2 = 2m|E|/\hbar^2$, which does not have a solution (one finds $A = B = 0$ from the conditions $\phi(a) = \phi(-a) = 0$).

For $E > 0$ one has solutions, which in general are of the form

$$\phi(x) = A\,\sin(kx) + B\,\cos(kx),$$

with $k^2 = 2mE/\hbar^2$, which leads to either $A = 0$ or $B = 0$. Check that the solutions separate into (including normalisation) the even solutions

$$\phi_n(x) = \frac{1}{\sqrt{a}}\cos\left(\frac{n\pi}{2a}\,x\right) \quad \text{with} \quad E_n = n^2\,\frac{\pi^2\hbar^2}{8ma^2} \quad (\text{odd } n \text{ values}), \tag{74}$$

and the odd solutions

$$\phi_n(x) = \frac{1}{\sqrt{a}}\sin\left(\frac{n\pi}{2a}\,x\right) \quad \text{with} \quad E_n = n^2\,\frac{\pi^2\hbar^2}{8ma^2} \quad (\text{even } n \text{ values}). \tag{75}$$

The number of nodes is given by $n - 1$. It is easy to check that the solutions are orthogonal,

$$\int_{-\infty}^{\infty} dx\ \phi_n^*(x)\,\phi_m(x) = \delta_{mn}. \tag{76}$$

3.4 Bound states and scattering solutions for a square well potential

We consider the potential

$$V(x) = -V_0 \quad \text{for } |x| < a \qquad \text{and} \qquad V(x) = 0 \quad \text{for } |x| \geq a.$$

One does not find a finite solution for $E < -V_0$. One would have exponential behavior in all x-ranges and since $k^2(x) < 0$ everywhere, one must have a solution which everywhere either has a positive or a negative derivative. For $-V_0 < E < V_0$, finite solutions are of the form

$$\phi(x) = C'\, e^{\kappa x} \quad \text{for } x \leq -a, \tag{77}$$

$$\phi(x) = A\, \sin(kx) + B\, \cos(kx) \quad \text{for } |x| \leq a, \tag{78}$$

$$\phi(x) = C\, e^{-\kappa x} \quad \text{for } x \geq a \tag{79}$$

(see Eq. 71), where $E = -\hbar^2\kappa^2/2m$ and $E + V_0 = \hbar^2 k^2/2m$. The matching conditions for wave functions and derivatives give

$$\begin{aligned} C'\, e^{-\kappa a} &= -A\, \sin(ka) + B\, \cos(ka), \\ A\, \sin(ka) + B\, \cos(ka) &= C\, e^{-\kappa a}, \\ (\kappa/k)\, C'\, e^{-\kappa a} &= A\, \cos(ka) + B\, \sin(ka), \\ A\, \cos(ka) - B\, \sin(ka) &= (\kappa/k)\, C\, e^{-\kappa a}. \end{aligned}$$

It is easy to convince one self that there are two classes of solutions,

- *even* solutions with $A = 0$ and $C' = C$,
- *odd* solutions with $B = 0$ and $C' = -C$.

For the solutions one obtains from the matching of logarithmic derivatives in the point $x = a$

$$k\, \tan(ka) = \kappa \qquad \text{(even)}, \tag{80}$$

$$k\, \cot(ka) = -\kappa \qquad \text{(odd)}. \tag{81}$$

Introducing the dimensionless variable $\xi = ka$ and writing $\xi_0 = \sqrt{2mV_0 a^2/\hbar^2}$, one has $\kappa a = \sqrt{\xi_0^2 - \xi^2}$ and $E = -\hbar^2\,(\xi_0^2 - \xi^2)/2ma^2$. The variable ξ runs from $0 \leq \xi \leq \xi_0$. The conditions become

$$\tan(\xi) = \frac{\sqrt{\xi_0^2 - \xi^2}}{\xi} \qquad \text{(even)}, \tag{82}$$

$$\tan(\xi) = -\frac{\xi}{\sqrt{\xi_0^2 - \xi^2}} \qquad \text{(odd)}. \tag{83}$$

One sees that there always is an even bound state in the region $0 \leq \xi \leq \text{minimum}\{\xi_0, \pi/2\}$, and then depending on the depth of the potential (i.e. as long as $\xi \leq \xi_0$) a first odd bound state (with one node) between $\pi/2 \leq \xi \leq \pi$, a second even bound state (with two nodes) between $\pi \leq \xi \leq 3\pi/2$, etc.

Next one might look for solutions with positive energy, in particular of the kind with boundary conditions as in Eqs. 69 and 70,

$$\phi(x) = e^{i\,kx} + A_R\, e^{-i\,kx} \quad \text{for } x \leq -a, \tag{84}$$

$$\phi(x) = A\, \sin(Kx) + B\, \cos(Kx) \quad \text{for } |x| \leq a, \tag{85}$$

$$\phi(x) = A_T\, e^{i\,kx} \quad \text{for } x \geq a, \tag{86}$$

where $E = \hbar^2 k^2/2m$ and $E + V_0 = \hbar^2 K^2/2m$. The matching conditions become

$$\begin{aligned} e^{-i\,ka} + A_R\, e^{i\,ka} &= -A\,\sin(Ka) + B\,\cos(Ka), \\ A\,\sin(Ka) + B\,\cos(Ka) &= A_T\, e^{i\,ka}, \\ i\,\frac{k}{K}\, e^{-i\,ka} - i\,A_R\,\frac{k}{K}\, e^{i\,ka} &= A\,\cos(Ka) + B\,\sin(Ka), \\ A\,\cos(Ka) - B\,\sin(Ka) &= i\,A_T\,\frac{k}{K}\, e^{i\,ka}. \end{aligned}$$

Eliminating A and B one obtains for the (complex) amplitudes of the reflected and transmitted waves,

$$A_R = e^{-2i\,ka}\,\frac{i(K^2 - k^2)\,\sin(2Ka)}{2kK\,\cos(2Ka) - i\,(k^2 + K^2)\,\sin(2Ka)}, \tag{87}$$

$$A_T = e^{-2i\,ka}\,\frac{2kK}{2kK\,\cos(2Ka) - i\,(k^2 + K^2)\,\sin(2Ka)}. \tag{88}$$

In contrast to negative energies, one has always solutions for positive energy. The interpretation of the specific ansatz of the wave function is an incoming wave from the left, $\phi_i(x) = e^{i\,kx}$ (with flux $j_i = k/m$), a reflected wave, $\phi_r(x) = A_R\, e^{-i\,kx}$ (with flux $j_r = -|A_R|^2\,k/m$), and a transmitted wave, $\phi_r(x) = A_T\, e^{i\,kx}$ (with flux $j_t = |A_T|^2\,k/m$). The probabilities for reflection and transmission are

$$\begin{aligned} R = |A_R|^2 &= \frac{(K^2 - k^2)^2\,\sin^2(2Ka)}{4k^2K^2\,\cos^2(2Ka) + (k^2 + K^2)^2\,\sin^2(2Ka)} \\ &= \frac{(K^2 - k^2)^2\,\sin^2(2Ka)}{4k^2K^2 + (K^2 - k^2)^2\,\sin^2(2Ka)} \end{aligned} \tag{89}$$

$$\begin{aligned} T = |A_T|^2 &= \frac{4k^2K^2}{4k^2K^2\,\cos^2(2Ka) + (k^2 + K^2)^2\,\sin^2(2Ka)} \\ &= \frac{4k^2K^2}{4k^2K^2 + (K^2 - k^2)^2\,\sin^2(2Ka)}, \end{aligned} \tag{90}$$

satisfying $1 - R = T$ (flux from the left = flux to the right). Note that there exists particular energies, for which the wave vector K satisfies $2Ka = n\pi$, in which case $R = 0$ and $T = 1$, i.e. the potential is 'invisible' for those particular waves.

3.5 Reflection and transmission through a barrier

We consider the situation of a positive square potential, also called a barrier potential,

$$V(x) = +V_0 \quad \text{for } |x| < a \qquad \text{and} \qquad V(x) = 0 \quad \text{for } |x| \ge a.$$

In this case we only have scattering solutions for $E > 0$. The case $E \ge V_0$ is even completely similar to the scattering solutions in the previous section. We have the same expression for $k^2 = 2mE/\hbar^2$, but now $K^2 = 2m(E - V_0)/\hbar^2$. The quantities k and K are the wave numbers in the different regions, respectively. In terms of k and K the expressions for reflection and transmission remain the same as in Eqs. 89 and 90. One again has the situation that there are energies for which $2Ka = n\pi$ and the barrier is 'invisible'.

The case $0 \le E \le V_0$ appears at first sight different because the wave functions in the region $-a \le x \le a$ become exponentional, e.g. linear combinations of $\cosh(\kappa x)$ and $\sinh(\kappa x)$ with $\kappa^2 = 2m(V_0 - E)/\hbar^2$. But this in fact is nothing else than using complex wave numbers, $K \to i\kappa$ (note that sign doesn't matter), leading instead of Eqs. 87 and 88 to

$$A_R = e^{-2i\,ka}\,\frac{-i\,(k^2+\kappa^2)\,\sinh(2\kappa a)}{2k\kappa\,\cosh(2\kappa a) - i\,(k^2-\kappa^2)\,\sin(2\kappa a)}, \tag{91}$$

$$A_T = e^{-2i\,ka}\,\frac{2k\kappa}{2k\kappa\,\cosh(2\kappa a) - i\,(k^2-\kappa^2)\,\sinh(2\kappa a)}. \tag{92}$$

leading to the reflection and transmission probabilities through a barrier,

$$R = |A_R|^2 = \frac{(k^2+\kappa^2)^2\,\sinh^2(2\kappa a)}{4k^2\kappa^2 + (k^2+\kappa^2)^2\,\sinh^2(2\kappa a)} \tag{93}$$

$$T = |A_T|^2 = \frac{4k^2\kappa^2}{4k^2\kappa^2 + (k^2+\kappa^2)^2\,\sinh^2(2\kappa a)}. \tag{94}$$

In this situation one always has $T < 1$. In the case that $\kappa a \gg 1$, which is the case if $E \ll V_0$ and $2m\,V_0\,a^2/\hbar^2 \gg 1$, the transmission coefficient reduces to the tiny probability

$$T \approx \frac{16\,k^2\kappa^2}{(k^2+\kappa^2)^2}\,e^{-4\kappa a} \approx 16\,\frac{E}{V_0}\,e^{-4\kappa a}.$$

In fact, only the exponential is the important part in this probability. For a barrier with a variable potential, the result becomes the famous WKB formula for tunneling, which is the product of the consecutive exponential factors for small barriers,

$$T \approx \exp\left(-2\int_{x_1}^{x_2} dx\,\left(\frac{2m}{\hbar^2}\right)^{1/2}\,[V(x)-E]^{1/2}\right), \tag{95}$$

where x_1 and x_2 are the points where $V(x_1) = V(x_2) = E$ with $V(x) \geq E$ in the region $x_1 \leq x \leq x_2$.

3.6 Three elementary properties of one-dimensional solutions

- In one dimension any attractive potential has always at least one bound state.
- For consecutive (in energy) solutions one has the *node theorem*, which states that the states can be ordered according to the number of nodes (zeros) in the wave function. The lowest energy solution has no node, the next has one node, etc.
- Bound state solutions of the one-dimensional Schrödinger equation are nondegenerate.

Proof: suppose that ϕ_1 and ϕ_2 are two solutions with the same energy. Construct

$$W(\phi_1,\phi_2) = \phi_1(x)\,\frac{d\phi_2}{dx} - \phi_2(x)\,\frac{d\phi_1}{dx}, \tag{96}$$

known as the Wronskian. It is easy to see that

$$\frac{d}{dx}\,W(\phi_1,\phi_2) = 0.$$

Hence one has $W(\phi_1,\phi_2) =$ constant, where the constant because of the asymptotic vanishing of the wave functions must be zero. Thus

$$\frac{(d\phi_1/dx)}{\phi_1} = \frac{(d\phi_2/dx)}{\phi_2} \quad\Rightarrow\quad \frac{d}{dx}\ln\phi_1 = \frac{d}{dx}\ln\phi_2$$

$$\Rightarrow\quad \frac{d}{dx}\ln\left(\frac{\phi_1}{\phi_2}\right) = 0 \quad\Rightarrow\quad \ln\left(\frac{\phi_1}{\phi_2}\right) = constant \quad\Rightarrow\quad \phi_1 \propto \phi_2,$$

and hence (when normalized) the functions are identical.

Appendix: Basic Knowledge

Basic relations between sin, cos, sinh, cosh and (complex) exponentials,

$$\sin x = \frac{e^{ix} - e^{-ix}}{2i} = -i\,\sinh(i\,x), \qquad \text{and} \qquad \cos x = \frac{e^{ix} + e^{-ix}}{2} = \cosh(i\,x),$$
$$\sinh x = \frac{e^{x} - e^{-x}}{2} = -i\,\sin(i\,x), \qquad \text{and} \qquad \cosh x = \frac{e^{x} + e^{-x}}{2} = \cos(i\,x),$$

and their behavior.

Questions

1. What is the behavior of wave functions in the region where $V(x) < E$, what in the region where $V(x) \geq E$. What are the explicit solutions for constant potentials?
2. Compare qualitatively the fall-off or wave lengths of wave functions with different energies.
3. Compare the wave lengths for the scattering solutions in the case of the attractive square well potential and the repulsive one (barrier).

Exercises

Exercise 3.1

(a) Use Mathematica to find the wave numbers $k_n a$ for the solutions of a square well potential for which $\xi_0 = \sqrt{2mV_0a^2/\hbar^2} = 7$.

(b). Compare the spectrum of wave numbers with that of the infinite square well.

Exercise 3.2

We investigate the wave function in the case of the potential step

$$V(x) = \begin{cases} V_0 & x \leq 0 \\ 0 & x > 0 \end{cases} .$$

(a) Give the possible solutions of the Schrödinger equation for negative and positive x for energies $0 \leq E \leq V_0$.

(b) Write the wave function for $x > 0$ as

$$\phi(x) = e^{-ikx} + A_R e^{+ikx},$$

calculate A_R and show that $|A_R| = 1$.

The phase shift δ of the reflected wave compared with the incoming wave is defined as

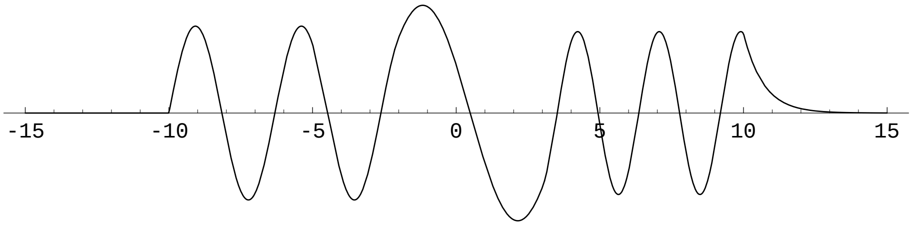
$$A_R \equiv -e^{2i\delta}.$$

(d) Rewrite the wave function as a sine with the phase shift in the argument. Calculate for a given energy E the phase shift $\delta(E)$ and sketch as a function of E/V_0.

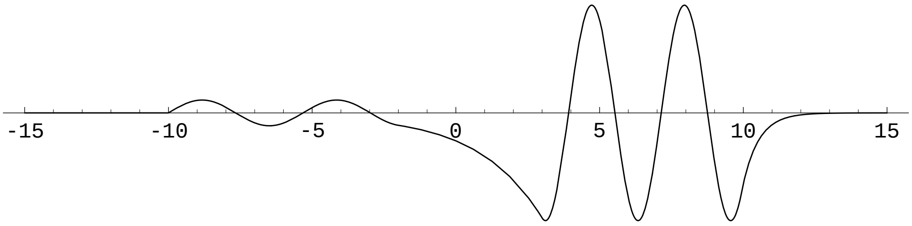
(e) Wat are A_R and the complete wave function in the limit $V_0 \to \infty$ and explain the result.

Exercise 3.3

Two wave functions with different energies are given below. These wave functions are both solutions of the same one-dimensional Schrödinger equation in a potential $V(x)$. This potential consists of step functions.



Wave function A



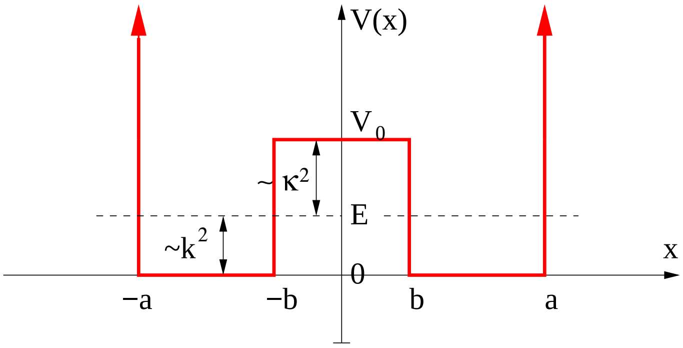
Wave function B

(a) Give a sketch of $V(x)$ and indicate the energy levels for the solutions A and B.

(b) How many wave functions belonging to $V(x)$ exist with energies lower than solution B? Sketch one of these wave functions.

Exercise 3.4

Given a one dimensional potential of the form in the figure



(a) Give the expressions for the wave functions in the various regions for the energy E indicated in the figure. We can just as for the square well distinguish even and odd solutions (since the potential is symmetric). This will considerably reduce the number of conditions.

(b) Sketch for both even and odd wave solutions the lowest one and give for each of these the matching conditions.

(c) If the potential for $|x| > a$ is equal to V_0, sketch then a solution for $E > V_0$ in such a way that it is clear what its behavior is in the various regions.

Exercise 3.5

Given a one-dimensional potential of the form

$$V(x) = -\frac{\hbar^2}{m\,a}\,\delta(x).$$

[See section 7.3 for the properties of the delta-function]

(a) Show that for a solution of the Schrödinger equation

$$\lim_{x\downarrow 0} \phi'(x) - \lim_{x\uparrow 0} \phi'(x) = -\frac{2\,\phi(0)}{a}.$$

(b) Show that there (always) exist one bound state solution. Give the wave function and the energy of this solution.

(c) Calculate for positive energies the transmission and reflection coefficient (A_T en A_R) for a wave coming from the left (from $x \rightarrow -\infty$).

(d) Show that the flux is conserved.

4 Angular momentum and spherical harmonics

In this section we study the (three) angular momentum operators $\hat{\boldsymbol{\ell}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}} = -i\hbar\, \boldsymbol{r} \times \boldsymbol{\nabla}$, looking for eigenvalues and eigenstates. The angular momentum operators are best studied in polar coordinates,

$$x = r\,\sin\theta\,\cos\varphi, \tag{97}$$
$$y = r\,\sin\theta\,\sin\varphi, \tag{98}$$
$$z = r\,\cos\theta, \tag{99}$$

from which one gets

$$\begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial \varphi} \end{pmatrix} = \begin{pmatrix} x/r & y/r & z/r \\ x\,\cot\theta & y\,\cot\theta & -r\,\sin\theta \\ -y & x & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix}.$$

The $\hat{\boldsymbol{\ell}}$ operators are given by

$$\hat{\ell}_x = -i\hbar\left(y\,\frac{\partial}{\partial z} - z\,\frac{\partial}{\partial y}\right) = i\hbar\left(\sin\varphi\,\frac{\partial}{\partial\theta} + \cot\theta\,\cos\varphi\,\frac{\partial}{\partial\varphi}\right), \tag{100}$$
$$\hat{\ell}_y = -i\hbar\left(z\,\frac{\partial}{\partial x} - x\,\frac{\partial}{\partial z}\right) = i\hbar\left(-\cos\varphi\,\frac{\partial}{\partial\theta} + \cot\theta\,\sin\varphi\,\frac{\partial}{\partial\varphi}\right), \tag{101}$$
$$\hat{\ell}_z = -i\hbar\left(x\,\frac{\partial}{\partial y} - y\,\frac{\partial}{\partial x}\right) = -i\hbar\,\frac{\partial}{\partial\varphi}, \tag{102}$$

and the square $\hat{\ell}^2$ becomes

$$\hat{\ell}^2 = \ell_x^2 + \ell_y^2 + \ell_z^2 = -\hbar^2\left[\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2}\right]. \tag{103}$$

From the expressions in polar coordinates, one immediately sees that the operators only acts on the angular dependence. One has $\hat{\ell}_i\, f(r) = 0$ for $i = x, y, z$ and thus also $\hat{\ell}^2\, f(r) = 0$. Being a simple differential operator (with respect to azimuthal angle about one of the axes) one has $\hat{\ell}_i(fg) = f\,(\hat{\ell}_i g) + (\hat{\ell}_i f)\,g$.

4.1 Spherical harmonics

We first study the action of the angular momentum operator on the Cartesian combinations x/r, y/r and z/r (only angular dependence). One finds

$$\hat{\ell}_z\,\left(\frac{x}{r}\right) = i\hbar\left(\frac{y}{r}\right), \qquad \hat{\ell}_z\,\left(\frac{y}{r}\right) = -i\hbar\left(\frac{x}{r}\right), \qquad \hat{\ell}_z\,\left(\frac{z}{r}\right) = 0,$$

which shows that the $\boldsymbol{\ell}$ operators acting on polynomials of the form

$$\left(\frac{x}{r}\right)^{n_1}\left(\frac{y}{r}\right)^{n_2}\left(\frac{z}{r}\right)^{n_3}$$

do not change the total degree $n_1 + n_2 + n_3 \equiv \ell$. They only change the degrees of the coordinates in the expressions. For a particular degree ℓ, there are $2\ell + 1$ functions. This is easy to see for $\ell = 0$ and $\ell = 1$. For $\ell = 2$ one must take some care and realize that $(x^2 + y^2 + z^2)/r^2 = 1$, i.e. there is one function less than the six that one might have expected at first hand. The symmetry of $\hat{\ell}^2$ in x, y and z immediately implies that polynomials of a particular total degree ℓ are eigenfunctions of $\hat{\ell}^2$ with the same eigenvalue $\hbar^2\,\lambda$.

Using polar coordinates one easily sees that eigenfunctions of ℓ_z,

$$\hat{\ell}_z\,Y(\theta,\varphi) = -i\hbar\,\frac{\partial}{\partial\varphi}\,Y(\theta,\varphi),$$

are of the form $Y_m(\theta,\varphi) = \Theta_m(\theta)\,e^{i\,m\varphi}$, where the actual eigenvalue is $m\hbar$ and in order that the eigenfunction is univalued m must be integer. For fixed degree ℓ of the polynomials m can at most be equal to ℓ, in which case the θ-dependence is $\sin^\ell\theta$. It is easy to calculate the $\hat{\ell}^2$ eigenvalue for this function, for which one finds $\hbar^2\ell(\ell+1)$. The rest is a matter of normalisation and convention and can be found in many books. Summarizing the eigenfunctions of $\boldsymbol{\ell}^2$ and ℓ_z, referred to as the spherical harmonics, are given by

$$\hat{\ell}^2\,Y_\ell^m(\theta,\varphi) = \ell(\ell+1)\hbar^2\,Y_\ell^m(\theta,\varphi), \tag{104}$$

$$\hat{\ell}_z\,Y_\ell^m(\theta,\varphi) = m\hbar\,Y_\ell^m(\theta,\varphi), \tag{105}$$

with the value $\ell = 0, 1, 2, \ldots$ and for given ℓ (called orbital angular momentum) $2\ell+1$ possibilities for the value of m (the magnetic quantum number), $m = -\ell, -\ell+1, \ldots, \ell$. Given one of the operators, $\boldsymbol{\ell}^2$ or ℓ_z, there are degenerate eigenfunctions, but with the eigenvalues of both operators one has a unique labeling (we will come back to this). Note that these functions are not eigenfunctions of ℓ_x and ℓ_y. Using kets to denote the states one uses $|\ell,m\rangle$ rather than $|Y_m^\ell\rangle$. From the polynomial structure, one immediately sees that the behavior of the spherical harmonics under space inversion ($\boldsymbol{r} \to -\boldsymbol{r}$) is determined by ℓ. This behavior under space inversion, known as the parity, of the Y_ℓ^m's is $(-)^\ell$.

The explicit result for $\ell = 0$ is

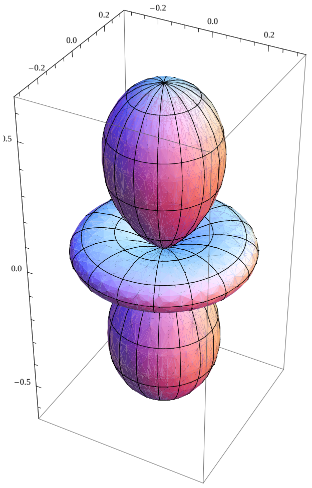
$$Y_0^0(\theta,\varphi) = \frac{1}{\sqrt{4\pi}}. \tag{106}$$

Explicit results for $\ell = 1$ are

$$Y_1^1(\theta,\varphi) = -\sqrt{\frac{3}{8\pi}}\,\frac{x+iy}{r} = -\sqrt{\frac{3}{8\pi}}\,\sin\theta\,e^{i\varphi}, \tag{107}$$

$$Y_1^0(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\,\frac{z}{r} = \sqrt{\frac{3}{4\pi}}\,\cos\theta, \tag{108}$$

$$Y_1^{-1}(\theta,\varphi) = \sqrt{\frac{3}{8\pi}}\,\frac{x-iy}{r} = \sqrt{\frac{3}{8\pi}}\,\sin\theta\,e^{-i\varphi}. \tag{109}$$



The $\ell = 2$ spherical harmonics are the (five!) quadratic polynomials of degree two,

$$Y_2^{\pm 2}(\theta,\varphi) = \sqrt{\frac{15}{32\pi}}\,\frac{(x^2-y^2)\pm 2i\,xy}{r^2} = \sqrt{\frac{15}{32\pi}}\,\sin^2\theta\,e^{\pm 2i\varphi}, \tag{110}$$

$$Y_2^{\pm 1}(\theta,\varphi) = \mp\sqrt{\frac{15}{8\pi}}\,\frac{z(x\pm iy)}{r^2} = \mp\sqrt{\frac{15}{8\pi}}\,\sin\theta\,\cos\theta\,e^{\pm i\varphi}. \tag{111}$$

$$Y_2^0(\theta,\varphi) = \sqrt{\frac{5}{16\pi}}\,\frac{3\,z^2-r^2}{r^2} = \sqrt{\frac{5}{16\pi}}\,\left(3\cos^2\theta - 1\right), \tag{112}$$

where the picture of $|Y_2^0|$ is produced using Mathematica, `SphericalPlot3D[Abs[SphericalHarmonicY[2,0,theta,phi]], {theta,0,Pi},{phi,0,2*Pi}]`.

The spherical harmonics form a complete set of functions on the sphere, satisfying the orthonormality relations

$$\int d\Omega\, Y_\ell^{m*}(\theta,\varphi)\, Y_{\ell'}^{m'}(\theta,\varphi) = \delta_{\ell\ell'}\,\delta_{mm'}. \tag{113}$$

Any function $f(\theta,\varphi)$ can be expanded in these functions,

$$f(\theta,\varphi) = \sum_{\ell,m} c_{\ell m}\, Y_\ell^m(\theta,\varphi),$$

with $c_{\ell m} = \int d\Omega\, Y_\ell^{m*}(\theta,\varphi)\, f(\theta,\varphi)$. Useful relations are the following,

$$Y_\ell^m(\theta,\varphi) = (-)^{(m+|m|)/2}\sqrt{\frac{2\ell+1}{4\pi}\,\frac{(\ell-|m|)!}{(\ell+|m|)!}}\,P_\ell^{|m|}(\cos\theta)\,e^{im\varphi}, \tag{114}$$

where $\ell = 0,1,2,\ldots$ and $m = \ell, \ell-1, \ldots, -\ell$, and the associated Legendre polynomials are given by

$$P_\ell^{|m|}(x) = \frac{1}{2^\ell\,\ell!}\,(1-x^2)^{|m|/2}\,\frac{d^{\ell+|m|}}{dx^{\ell+|m|}}\,\left[(x^2-1)^\ell\right]. \tag{115}$$

The $m = 0$ states are related to the (orthogonal) Legendre polynomials, $P_\ell = P_\ell^0$, given by

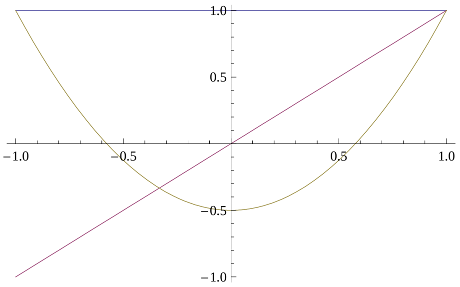
$$P_\ell(\cos\theta) = \sqrt{\frac{4\pi}{2\ell+1}}\,Y_\ell^0(\theta). \tag{116}$$

They are defined on the $[-1,1]$ interval. They can be used to expand functions that only depend on θ (see chapter on scattering theory).

The lowest order Legendre polynomials $P_n(x)$ (`LegendreP[n,x]`) are

$$P_0(x) = 1,$$
$$P_1(x) = x,$$
$$P_2(x) = \frac{1}{2}(3x^2-1)$$

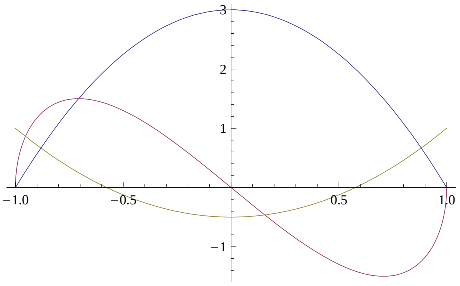
(given in the figure to the right).



Some of the associated Legendre polynomials $P_n^m(x)$ (`LegendreP[n,m,x]`) are

$$P_1^1(x) = -\sqrt{1-x^2},$$
$$P_2^1(x) = -3x\sqrt{1-x^2},$$
$$P_2^2(x) = 3\,(1-x^2)$$

(shown in the figure $P_2^m(x)$ for $m = 0$, 1 en 2).

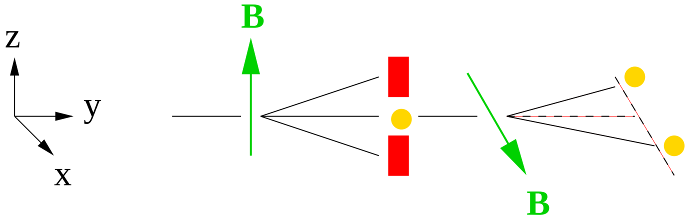


4.2 Measuring angular momentum and the Stern-Gerlach experiment

Measurements in quantum mechanics can be splendidly illustrated with angular momentum, which classically is a continuous variable and quantummechanically is an operator with discrete eigenvalues. The type of experiments are usually referred to as Stern-Gerlach experiment, although the original experiment is different from our discussion below.

A charged particle (say an electron with charge $-e$) with angular momentum $\boldsymbol{\ell}$ has a magnetic moment $\boldsymbol{\mu} = -(e/2m)\,\boldsymbol{\ell}$. In a magnetic field the interaction energy is $U = \boldsymbol{\mu} \cdot \boldsymbol{B}$. In a varying magnetic field the particle experiences a force $\boldsymbol{F} = -\boldsymbol{\nabla}(\boldsymbol{\mu} \cdot \boldsymbol{B})$ proportional to ℓ_B, where ℓ_B is the component of ℓ along B. Classically the effect is a continuous spreading of the electrons. Quantummechanically, we have seen that the eigenvalues of ℓ_z (let's choose $\boldsymbol{B}$ along the z-axis) are $m\hbar$ with m integer, thus depending on (the gradient of) $\boldsymbol{B}$ a discrete set of possibilities.

Let's consider the example of $\ell = 1$. There are three possible eigenvalues of ℓ_z with m = -1, 0, or 1. Thus starting with a beam of electrons with no prejudice (equal amounts of all states) the Stern-Gerlach apparatus with $\boldsymbol{B}$ along the z-axis (a measurement of ℓ_z) produces 3 beams (see figure).



The state in each of the beams is described by a wave function for which the angular momentum part is $\propto Y_1^m(\theta,\varphi)$. Let us denote these states with $\psi_m^{(z)}$. Summarizing this with

$$\text{state} \rightarrow \boxed{\text{measurement}} \rightarrow \text{eigenvalue} \rightarrow \text{state}$$

we have

$$\psi \rightarrow \boxed{\ell_z} \rightarrow \begin{cases} \ell_z = 1\,\hbar & \rightarrow \psi_1^{(z)} \sim -(x+i\,y)/\sqrt{2} \\ \ell_z = 0 & \rightarrow \psi_0^{(z)} \sim z \\ \ell_z = -1\,\hbar & \rightarrow \psi_{-1}^{(z)} \sim (x-i\,y)/\sqrt{2} \end{cases}$$

We can now (as in the figure) block two of the beams and perform a different measurement, e.g. of ℓ_x (rotating the apparatus). The result of the measurement is a splitting into two beams, as postulated for a quantum mechanical measurement. Namely we get as a result of the measurement the possible eigenvalues of ℓ_x, again $m\hbar$ with m = -1, 0, or 1. To determine the probabilities in the beam, we have to decompose the wave function z/r into eigenfunctions $\psi_m^{(x)}$ of ℓ_x. Symmetry considerations show that

$$\psi_1^{(x)} \sim -(y+i\,z)/\sqrt{2} \qquad \psi_0^{(x)} \sim x \qquad \psi_{-1}^{(x)} \sim (y-i\,z)/\sqrt{2},$$

Decomposing

$$z = \frac{1}{i\sqrt{2}}\,\frac{y+i\,z}{\sqrt{2}} - \frac{1}{i\sqrt{2}}\,\frac{y-i\,z}{\sqrt{2}},$$

gives coefficients $\pm i/\sqrt{2}$. Squaring leads to probabilities 1/2. Thus after the second measurement the beam splits into two beams with equal probabilities. Thus:

$$\psi \sim z \rightarrow \boxed{\ell_x} \rightarrow \begin{cases} \ell_x = 1\,\hbar & 50\% & \rightarrow \psi_1^{(x)} \sim -(y+i\,z)/\sqrt{2} \\ \ell_x = 0 & 0\% & \rightarrow \psi_0^{(x)} \sim x \\ \ell_x = -1\,\hbar & 50\% & \rightarrow \psi_{-1}^{(x)} \sim (y-i\,z)/\sqrt{2} \end{cases}$$

4.3 The radial Schrödinger equation in three dimensions

In three dimensions the eigenstates of the Hamiltonian for a particle in a potential are found from

$$H\,\psi(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\boldsymbol{r})\right]\psi(\boldsymbol{r}) = E\,\psi(\boldsymbol{r}). \tag{117}$$

In particular in the case of a central potential, $V(\boldsymbol{r}) = V(r)$ it is convenient to use spherical coordinates. Introducing polar coordinates one has

$$\begin{aligned} \boldsymbol{\nabla}^2 &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\,\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\,\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} && (118)\\ &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\boldsymbol{\ell}^2}{\hbar^2\,r^2}. && (119)\end{aligned}$$

where $\boldsymbol{\ell}$ are the three angular momentum operators. If the potential has no angular dependence, the eigenfunctions can be written as

$$\psi_{n\ell m}(\boldsymbol{r}) = R_{n\ell m}(r)\,Y_\ell^m(\theta,\varphi). \tag{120}$$

Inserting this in the eigenvalue equation one obtains

$$\left[-\frac{\hbar^2}{2m\,r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \left(\frac{\hbar^2\,\ell(\ell+1)}{2m\,r^2} + V(r)\right)\right]R_{n\ell}(r) = E_{n\ell}\,R_{n\ell}(r), \tag{121}$$

in which the radial function R and energy E turn out to be independent of the magnetic quantum number m.

In order to investigate the behavior of the wave function for $r \to 0$, let us assume that near zero one has $R(r) \sim C\,r^s$. Substituting this in the equation one finds for a decent potential ($\lim_{r\to 0} r^2\,V(r) = 0$) immediately that $s(s+1) = \ell(\ell+1)$, which allows two types of solutions, namely $s = \ell$ (*regular* solutions) or $s = -(\ell+1)$ (*irregular* solutions). The irregular solutions cannot be properly normalized and are rejected[3].

For the regular solutions, it is convenient to write

$$\psi(\boldsymbol{r}) = R(r)\,Y_\ell^m(\theta,\varphi) = \frac{u(r)}{r}\,Y_\ell^m(\theta,\varphi). \tag{122}$$

Inserting this in the eigenvalue equation for R one obtains the radial Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \underbrace{\frac{\hbar^2\,\ell(\ell+1)}{2m\,r^2} + V(r)}_{V_{\text{eff}}(r)} - E_{n\ell}\right]u_{n\ell}(r) = 0, \tag{123}$$

with boundary condition $u_{n\ell}(0) = 0$, since $u(r) \sim C\,r^{\ell+1}$ for $r \to 0$. This is simply a one-dimensional Schrödinger equation on the positive axis with a boundary condition at zero and an effective potential consisting of the central potential and an angular momentum barrier.

---

[3] Actually, in the case $\ell = 0$, the irregular solution $R(r) \sim 1/r$ is special. One might say that it could be normalized, but we note that it is not a solution of $\boldsymbol{\nabla}^2 R(r) = 0$, rather one has $\boldsymbol{\nabla}^2\frac{1}{r} = \delta^3(\boldsymbol{r})$ as may be known from courses on electricity and magnetism.

Questions

1. Considering the Y_ℓ^m as polynomials of degree ℓ, argue why the ℓ_z eigenvalue m can be at most ℓ.

Exercises

Exercise 4.1

(a) Show that the functions $\sin^\ell \theta \, e^{\pm i\ell\phi}$ are eigenfunctions of $\hat{\ell}^2$ with eigenvalue $\hbar^2 \, \ell(\ell+1)$.

(b) Normalize this solution.

Exercise 4.2

Describe the measurement of ℓ_y in section 4.2 if we let the beam with $\ell_z = -\hbar$ pass after the first measurement.

Exercise 4.3

Consider a 'square well' potential in three dimensions with $V(\boldsymbol{r}) = -V_0$ if $r = |\boldsymbol{r}| \le a$ and $V(\boldsymbol{r}) = 0$ if $r > a$.

(a) Find the condition for s-wave ($\ell = 0$) bound state solutions (with $E = -\hbar^2\,\kappa^2/2m \le 0$).

(b) Show that the condition to have at least one bound state is $V_0\,a^2 \ge \pi^2\hbar^2/8m$. Note that this condition can be derived without using the result of (a).

Exercise 4.4

(a) Derive the Schrödinger equation in cylindrical coordinates (ρ, ϕ, z), following the steps for spherical coordinates, starting with

$$\begin{aligned} x &= \rho\,\cos\varphi, \\ y &= \rho\,\sin\varphi, \\ z &= z. \end{aligned}$$

(b) Give the most general solution for a cylindrically symmetric potential only depending on ρ, using eigenfunctions of $p_z = -i\hbar\,\partial/\partial z$ and $\ell_z = -i\hbar\,\partial/\partial\varphi$ and give the Schrödinger equation that determines the ρ-dependence. Try to simplify this into a 'one-dimensional' Schrödinger equation.

5 The hydrogen atom

5.1 Transformation to the center of mass

For a hydrogen-like atom, one starts with the hamiltonian for the nucleus with charge $+Ze$ (mass m_N) and the electron with charge $-e$ (mass m_e),

$$H = -\frac{\hbar^2}{2m_N}\boldsymbol{\nabla}_p^2 - \frac{\hbar^2}{2m_e}\boldsymbol{\nabla}_e^2 - \frac{Ze^2}{4\pi\epsilon_0\,|\boldsymbol{r}_e - \boldsymbol{r}_p|}. \tag{124}$$

This can using total mass $M = m_e + m_N$ and reduced mass $m = m_e m_N/M$ be rewritten in terms of the center of mass and relative coordinates,

$$M\boldsymbol{R} = m_N\boldsymbol{r}_N + m_e\boldsymbol{r}_e, \tag{125}$$

$$\boldsymbol{r} = \boldsymbol{r}_e - \boldsymbol{r}_N, \tag{126}$$

and dito momenta

$$\boldsymbol{P} = \boldsymbol{p}_e + \boldsymbol{p}_N = -i\hbar\boldsymbol{\nabla}_R, \tag{127}$$

$$\frac{\boldsymbol{p}}{m} = \frac{\boldsymbol{p}_e}{m_e} - \frac{\boldsymbol{p}_N}{m_N} = -i\hbar\boldsymbol{\nabla}_r. \tag{128}$$

One obtains

$$H = \underbrace{-\frac{\hbar^2}{2M}\boldsymbol{\nabla}_R^2}_{H_{\rm cm}}\underbrace{-\frac{\hbar^2}{2m}\boldsymbol{\nabla}_r^2 - \frac{Ze^2}{4\pi\epsilon_0\, r}}_{H_{\rm rel}}. \tag{129}$$

The hamiltonian is separable, the eigenfunction $\psi_E(\boldsymbol{R}, \boldsymbol{r})$ is the product of the solutions $\psi_{E_{\rm cm}}(\boldsymbol{R})$ of $H_{\rm cm}$ and $\psi_{E_{\rm rel}}(\boldsymbol{r})$ of $H_{\rm rel}$, while the eigenvalue is the sum of the eigenvalues. In particular one knows that $\psi_{E_{\rm cm}}(\boldsymbol{R}) = \exp(i\,\boldsymbol{P}\cdot\boldsymbol{R})$ with $E_{\rm cm} = \boldsymbol{P}^2/2M$, leaving a one-particle problem in the relative coordinate $\boldsymbol{r}$ for a particle with reduced mass m.

5.2 Solving the eigenvalue equation

The (one-dimensional) radial Schrödinger equation for the relative wave function in the Hydrogen atom reads

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \underbrace{\frac{\hbar^2\,\ell(\ell+1)}{2m\,r^2} + V_c(r)}_{V_{\rm eff}(r)} - E\right]u_{n\ell}(r) = 0, \tag{130}$$

with boundary condition $u_{n\ell}(0) = 0$. First of all it is useful to make this into a dimensionless differential equation for which we then can use our knowledge of mathematics. Define $\rho = r/a_0$ with for the time being a_0 still unspecified. Multiplying the radial Schrödinger equation with $2m\,a_0^2/\hbar^2$ we get

$$\left[-\frac{d^2}{d\rho^2} + \frac{\ell(\ell+1)}{\rho^2} - \frac{e^2}{4\pi\epsilon_0}\frac{2m\,a_0}{\hbar^2}\frac{Z}{\rho} - \frac{2m\,a_0^2\,E}{\hbar^2}\right]u_{E\ell}(\rho) = 0. \tag{131}$$

From this dimensionless equation we find that the coefficient multiplying $1/\rho$ is a number. Since we haven't yet specified a_0, this is a good place to do so and one defines the *Bohr radius*

$$a_0 \equiv \frac{4\pi\epsilon_0\,\hbar^2}{m\,e^2}. \tag{132}$$

The stuff in the last term in the equation multiplying E must be of the form 1/energy. One defines the *Rydberg energy*

$$R_\infty = \frac{\hbar^2}{2m\,a_0^2} = \frac{1}{2}\,\frac{e^2}{4\pi\epsilon_0\,a_0} = \frac{m\,e^4}{32\pi^2\epsilon_0^2\,\hbar^2}. \tag{133}$$

One then obtains the dimensionless equation

$$\left[-\frac{d^2}{d\rho^2} + \frac{\ell(\ell+1)}{\rho^2} - \frac{2Z}{\rho} - \epsilon\right] u_{\epsilon\ell}(\rho) = 0 \tag{134}$$

with $\rho = r/a_0$ and $\epsilon = E/R_\infty$.

Before solving this equation let us look at the magnitude of the numbers with which the energies and distances in the problem are compared. Using the dimensionless fine structure constant one can express the distances and energies in the electron Compton wavelength,

$$\alpha = \frac{e^2}{4\pi\,\epsilon_0\,\hbar c} \approx 1/137, \tag{135}$$

$$a_0 \equiv \frac{4\pi\epsilon_0\,\hbar^2}{m\,e^2} = \frac{4\pi\epsilon_0\,\hbar c}{e^2}\,\frac{\hbar c}{mc^2} = \frac{1}{\alpha}\,\frac{\hbar c}{mc^2} \approx 0.53\times 10^{-10}\ \text{m}, \tag{136}$$

$$R_\infty = \frac{\hbar^2}{2m\,a_0^2} = \frac{1}{2}\,\alpha\left(\frac{\hbar c}{a_0}\right) = \frac{1}{2}\,\alpha^2\,mc^2 \approx 13.6\ \text{eV}. \tag{137}$$

One thing to be noticed is that the defining expressions for a_0 and R_∞ involve the electromagnetic charge $e/\sqrt{\epsilon_0}$ and Planck's constant $\hbar$, but it does not involve c. The hydrogen atom invokes quantum mechanics, but not relativity! The nonrelativistic nature of the hydrogen atom is confirmed in the characteristic energy scale being R_∞. We see that it is of the order $\alpha^2 \sim 10^{-4} - 10^{-5}$ of the restenergy of the electron, i.e. very tiny!

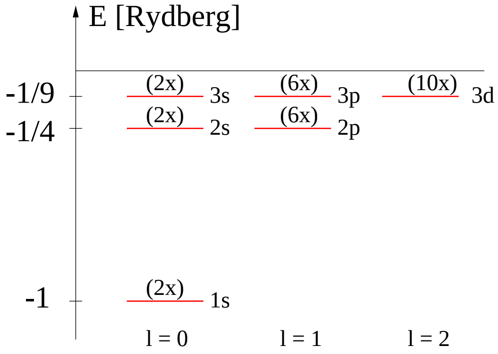
To find the solutions in general, we can turn to an algebraic manipulation program or a mathematical handbook to look for the solutions of the dimensionless differential equation (see subsection on Laguerre polynomials). We see from this treatment that (using $p \to n-\ell-1$, $a \to 2\ell+1$ and $x \to 2Z\rho/n$) the solutions for hydrogen are

$$u_{n\ell}(\rho) = \left(\frac{2Z}{n\,a_0}\right)^{1/2}\sqrt{\frac{(n-\ell-1)!}{2n\,(n+\ell)!}}\;e^{-Z\rho/n}\left(\frac{2Z\rho}{n}\right)^{\ell+1} L_{n-\ell-1}^{2\ell+1}\left(\frac{2Z\rho}{n}\right) \tag{138}$$

with eigenvalues (energies)

$$E_{n\ell} = -\frac{Z^2}{n^2}\,R_\infty, \tag{139}$$

labeled by a principal quantum number number n, choosen such that the energy only depends on n. For a given ℓ one has $n \geq \ell+1$. Actually $n_r = n-\ell-1$ is the number of nodes in the wave function.



The spectrum of the hydrogen atom. For a given n one has degenerate ℓ-levels with $\ell = 0, 1, \ldots, n-1$. The degeneracy, including the electron spin, adds up to $2n^2$. The hamiltonian is invariant under inversion, hence its eigenstates are also parity eigenstates. The parity of ψ_{nlm} is given by $\Pi = (-)^\ell$.

Some aspects of the solution can be easily understood. For instance, looking at equation 134 one sees that the asymptotic behavior of the wave function is found from

$$u''(\rho) + \epsilon\, u(\rho) = 0,$$

so one expects for $\rho \to \infty$ the result $u(\rho) \sim e^{-\rho\sqrt{|\epsilon|}}$. For $\ell = 0$ one expects for $\rho \to 0$ that $u(\rho) \sim \rho$. Indeed it is easy to check that $u_{10}(\rho) \sim \rho\, e^{-Z\rho}$ is a solution with $\epsilon = -Z^2$.

Explicitly, the lowest solutions are:

$$u_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/a_0}\left(\frac{Zr}{a_0}\right), \tag{140}$$

$$u_{20}(r) = \frac{1}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/2a_0}\left(\frac{Zr}{a_0}\right)\left(1 - \frac{1}{2}\frac{Zr}{a_0}\right) \tag{141}$$

$$u_{21}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/2a_0}\left(\frac{Zr}{a_0}\right)^2 \tag{142}$$

$$u_{30}(r) = \frac{2}{3\sqrt{3}}\left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/3a_0}\left(\frac{Zr}{a_0}\right)\left(1 - \frac{2}{3}\frac{Zr}{a_0} + \frac{2}{27}\left(\frac{Zr}{a_0}\right)^2\right) \tag{143}$$

$$u_{31}(r) = \frac{8}{27\sqrt{6}}\left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/3a_0}\left(\frac{Zr}{a_0}\right)^2\left(1 - \frac{1}{6}\frac{Zr}{a_0}\right) \tag{144}$$

$$u_{32}(r) = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/3a_0}\left(\frac{Zr}{a_0}\right)^3 \tag{145}$$

Useful integrals involving the solutions are expectation values like

$$\langle\frac{r^2}{a_0^2}\rangle = \frac{n^2}{2Z^2}\left[5n^2 - 3\,\ell(\ell+1) + 1\right], \tag{146}$$

$$\langle\frac{r}{a_0}\rangle = \frac{1}{2Z}\left[3\,n^2 - \ell(\ell+1)\right], \tag{147}$$

$$\langle\frac{a_0}{r}\rangle = \frac{Z}{n^2}, \tag{148}$$

$$\langle\frac{a_0^2}{r^2}\rangle = \frac{2\,Z^2}{n^3(2\ell+1)}, \tag{149}$$

$$\langle\frac{a_0^3}{r^3}\rangle = \frac{2\,Z^3}{n^3\,\ell(\ell+1)(2\ell+1)}. \tag{150}$$

The full hamiltonian for the Hydrogen atom has a number of additional terms, which give rise to splittings in the spectrum. These level splittings give rise to splitting of lines in emission and absorption spectra. Some of the fine structure and hyperfine structure will be discussed after the treatment of spin or as applications of perturbation theory.

5.3 Appendix: Generalized Laguerre polynomials

For the solution of a dimensionless equation such as that for the Hydrogen atom we can turn to an algebraic manipulation program or a mathematical handbook. The solutions of the equation

$$y'' + g_0(x)\,y = 0 \qquad \text{with} \quad g_0(x) = \left[\frac{2p+a+1}{2x} + \frac{1-a^2}{4x^2} - \frac{1}{4}\right], \tag{151}$$

are given by

$$y(x) = e^{-x/2}\, x^{(a+1)/2}\, L_p^a(x). \tag{152}$$

where L_p^a are polynomials of degree p. They are normalized as

$$\int_0^\infty dx\; x^{a+1}\, e^{-x}\, \left[L_p^a(x)\right]^2 = (2p+a+1)\,\frac{(p+a)!}{p!}, \tag{153}$$

and also satisfy the differential equation

$$\left[x\,\frac{d^2}{dx^2} + (a+1-x)\,\frac{d}{dx} + p\right] L_p^a(x) = 0. \tag{154}$$

Note that depending on books, different conventions are around, differing in the indices of the polynomials, the normalization, etc. Some useful properties are

$$L_p(x) \equiv L_p^0(x) = \frac{e^x}{p!}\,\frac{d^p}{dx^p}\left[x^p\, e^{-x}\right] = \frac{1}{p!}\left(\frac{d}{dx} - 1\right)^p x^p, \tag{155}$$

$$L_p^a(x) = (-)^a\,\frac{d^a}{dx^a}\left[L_{p+a}(x)\right]. \tag{156}$$

Some general expressions are

$$L_0^a(x) = 1, \qquad L_1^a(x) = 1 + a - x.$$

Some recursion relations are

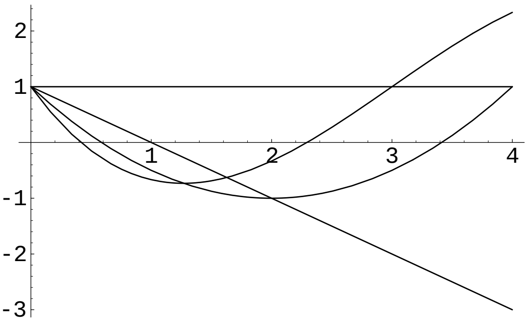
$$(p+1)\, L_{p+1}^a(x) = (2p+a+1-x)\, L_p^a(x) - (p+a)\, L_{p-1}^a(x), \tag{157}$$

$$x\, L_p^{a+1}(x) = (x-p)\, L_p^a(x) + (p+a)\, L_{p-1}^a(x), \tag{158}$$

$$L_p^a(x) = L_p^{a-1}(x) + L_{p-1}^a(x). \tag{159}$$

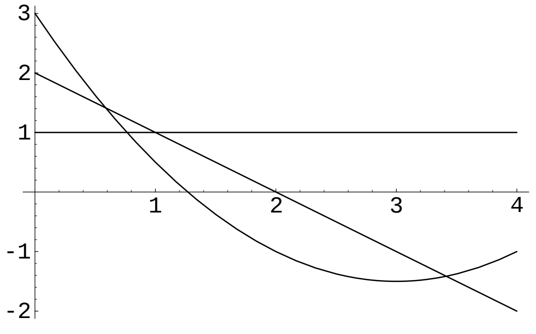
Some explicit polynomials are

$$\begin{aligned} L_0(x) &= 1, \\ L_1(x) &= 1 - x, \\ L_2(x) &= 1 - 2x + \frac{1}{2}\,x^2, \\ L_3(x) &= 1 - 3x + \frac{3}{2}\,x^2 - \frac{1}{6}\,x^3, \end{aligned}$$



The $L_p(x)$ or `LaguerreL[p,x]` functions for p = 0, 1, 2, and 3.

$$\begin{aligned} L_0^1(x) &= 1, \\ L_1^1 &= 2\left(1 - \frac{1}{2}\,x\right), \\ L_2^1(x) &= 3\left(1 - x + \frac{1}{6}\,x^2\right). \end{aligned}$$



The $L_p^a(x)$ or `LaguerreL[p,a,x]` functions for a = 1 and p = 0, 1, and 2.

5.4 A note on Bohr quantization

The model of Bohr of the atom imposes quantization in an ad hoc way by requiring $\ell = n\,\hbar$ with n being integer. For the electron in the atom one uses the condition that the central force to bind the electron is provided by the Coulomb attraction,

$$\frac{mv^2}{r} = \frac{Z\,e^2}{4\pi\epsilon_0\,r^2}, \tag{160}$$

We can solve this for classical (circular) orbits and find

$$\begin{aligned} E(r) &= \frac{1}{2}\,mv^2 - \frac{Z\,e^2}{4\pi\epsilon_0\,r} = -\frac{1}{2}\,\frac{Z\,e^2}{4\pi\epsilon_0\,r}, \\ \ell^2(r) &= m^2v^2r^2 = Z\,r\,\frac{m\,e^2}{4\pi\epsilon_0} \end{aligned}$$

Using the quantization condition on ℓ to eliminate v one finds

$$r_n = \frac{n^2}{Z}\,\frac{4\pi\epsilon_0\,\hbar^2}{m\,e^2}, \tag{161}$$

$$E_n = \frac{Z^2}{n^2}\,\frac{m\,e^4}{32\pi\epsilon_0^2\hbar^2}, \tag{162}$$

which turns out to give the correct (quantized) energy levels and also a good estimate of the radii. At the classical level the Sommerfeld model of the atom even includes quantization conditions for treating elliptical orbits.

It is interesting to observe that the Bohr quantization condition not only gives the right characteristic size (a_0) and energy (R_∞) and the right power dependence on quantities like Z, but what is more surprising also the right power behavior of the quantum numbers (n, ℓ). Note e.g. that the Bohr model gives $r \propto n^2$ and (indeed) all the expectation values involving r^p have a polynomial behavior in (n, ℓ) of order $2p$.

Exercises

Exercise 5.1

In this exercise the orthonormal eigenfunctions of the hamiltonian of the Hydrogen atoma are written as $|n\ell m\rangle$. Assume a particular Hydrogen atom is described by

$$|\psi\rangle = C\left(2|100\rangle + 3|211\rangle - 4|210\rangle + |21{-}1\rangle\right)\ .$$

Calculate the expectation values of the hamiltonian, $\boldsymbol{\ell}^2$ and ℓ_z. Which values of ℓ_z can be measured with what probabilities?

Exercise 5.2

(a) In general an operator, e.g. the Hamiltonian depends on some parameters (e.g. mass m, charge Z, ...), denote this as $H(\alpha)$. Show that if ϕ_n is an eigenfunction of H, $H|\phi_n\rangle = E_n|\phi_n\rangle$, one has

$$\langle\phi_n|\frac{\partial H}{\partial\alpha}|\phi_n\rangle = \frac{\partial E_n}{\partial\alpha}.$$

This is referred to as parametric parametrization. Note that not only H and E_n, but also $|\phi_n\rangle$ depend on the parameters α.

(b) Use parametric differentiation to find the expectation values $\langle 1/r\rangle_{n\ell}$ and $\langle \boldsymbol{p}^2\rangle_{n\ell}$ in Hydrogen-like atoms.

(c) Calculate the average velocity $\sqrt{\langle v^2\rangle_{n\ell}}$ and show the nonrelativistic nature of the Hydrogen atom.

Exercise 5.3

(a) Apply Bohr quantization to a gravitationally bound system. Estimate the quantum number for the orbit of the Earth around the Sun.

(b) Apply Bohr quantization to the harmonic oscillator (potential $\propto r^2$, see section 6.3) and the linear potential ($V(r) = T_0\, r$) and determine E_n and r_n.

Exercise 5.4

Investigate the asymptotic ($r \to \infty$) behavior of the radial wave function for bound states in a potential $V(r) \to C\, r^{\alpha}$ with $\alpha > -2$.
Show first that the asymptotic radial Schrödinger equation can be written in the following dimensionless form

$$u''(\xi) = (\xi^{\alpha} - \epsilon)\, u(\xi)$$

where $\xi = r/r_0$ and $\epsilon = E/E_0$ with

$$r_0 = \left(\frac{\hbar^2}{2m\,C}\right)^{\frac{1}{2+\alpha}} \qquad \text{and} \qquad E_0 = \frac{\hbar^2}{2m\, r_0^2}.$$

Next consider separately the cases $-2 < \alpha < 0$ and $\alpha > 0$.

Exercise 5.5

As a starting point for the solution of the Hydrogen atom we can use

$$u_{n\ell}(\rho) = \rho^{\ell+1}\, e^{-\rho\sqrt{|\epsilon|}} \sum_{k=0}^{n_r} c_k\, \rho^k.$$

where n_r is the number of nodes.

(a) What are the (general) arguments that allow this ansatz.

(b) Insert the ansatz in the Schrödinger equation and show that $\epsilon = -Z/(n_r + \ell + 1)^2 \equiv -Z/n^2$. Furthermore you can derive recursion relations for the coefficients. Note that one coefficient should be fixed first to calculate the others, e.g. $c_0 = 1$. The normalization of the wave function can be used afterwards to determine this coefficient.

6 The harmonic oscillator

6.1 The one-dimensional harmonic oscillator

The Schrödinger equation for the harmonic oscillator in one dimension is written as

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}\,m\omega^2\,x^2\right]\phi(x)=E\phi(x). \tag{163}$$

The harmonic oscillator potential is encountered in very many applications. It is a natural approximation for a system in equilibrium. Around the minimum of any potential function one can write

$$V(x)=V(x_{\rm min})+\frac{1}{2}\,k\,(x-x_{\rm min})^2+\ldots,$$

and after a redefinition of the energy (shift) and the coordinates (choose $x_{\rm min}=0$), one has $V(x)=\frac{1}{2}\,k\,x^2\equiv\frac{1}{2}\,m\omega^2\,x^2$.

The equation is made dimensionless by introducing $\xi=\alpha\,x$, leading to

$$\left[-\frac{\hbar^2\alpha^2}{2m}\frac{d^2}{d\xi^2}+\frac{m\omega^2}{2\,\alpha^2}\,\xi^2\right]\phi(\xi)=E\,\phi(\xi).$$

To fix α one can equate

$$\frac{\hbar^2\alpha^2}{m}=\frac{m\omega^2}{\alpha^2}\qquad\Longrightarrow\qquad\alpha^2=\frac{m\omega}{\hbar},$$

leading to

$$\left[-\frac{1}{2}\,\hbar\omega\,\frac{d^2}{d\xi^2}+\frac{1}{2}\,\hbar\omega\,\xi^2\right]\phi(\xi)=E\,\phi(\xi).$$

or with $\epsilon\equiv E/\hbar\omega$,

$$\left[-\frac{1}{2}\frac{d^2}{d\xi^2}+\frac{1}{2}\,\xi^2-\epsilon\right]\phi(\xi)=0 \tag{164}$$

One can now turn to a mathematics handbook (see appendix below). Actually one also can find the solutions starting from the lowest one. It is easy to check that

$$\phi_0(\xi)=e^{-\xi^2/2}, \tag{165}$$

is a solution with $\epsilon_0=1/2$. Since the function has no nodes it must be the lowest one. Using the fact that

$$\left(-\frac{d^2}{d\xi^2}+\xi^2-2\,\epsilon\right)\left(\frac{d}{d\xi}-\xi\right)\phi-\left(\frac{d}{d\xi}-\xi\right)\left(-\frac{d^2}{d\xi^2}+\xi^2-2\,\epsilon\right)\phi=2\left(\frac{d}{d\xi}-\xi\right)\phi,$$

and applying it to solution ϕ_n one sees that

$$\left(-\frac{d^2}{d\xi^2}+\xi^2-2\,\epsilon_n\right)\left(\frac{d}{d\xi}-\xi\right)\phi_n=2\left(\frac{d}{d\xi}-\xi\right)\phi_n,$$

which implies a new solution (next one in energy since it has one more node)

$$\phi_{n+1}(x)=\left(\frac{d}{d\xi}-\xi\right)\phi_n\qquad\text{with}\quad\epsilon_{n+1}=\epsilon_n+1.$$

Starting with the lowest one has

$$\phi_n(\xi)=\left(\xi-\frac{d}{d\xi}\right)^n e^{-\xi^2/2}\equiv H_n(\xi)\,e^{-\xi^2/2}, \tag{166}$$

with $\epsilon_n=(n+\frac{1}{2})$. Note that the parity of these solutions is $\phi_n(-\xi)=(-)^n\,\phi_n(\xi)$.

6.2 Appendix: Hermite polynomials

The problem of the one-dimensional harmonic oscillator in essence reduces to the differential equation

$$y'' + g_0(x)\, y = 0 \qquad \text{with} \quad g_0(x) = 2n + 1 - x^2 \tag{167}$$

for which the solutions are given by

$$y(x) = e^{-x^2/2}\, H_n(x). \tag{168}$$

where H_n are polynomials of degree n. They are normalized as

$$\int_{-\infty}^{\infty} dx\ e^{-x^2}\, [H_n(x)]^2 = 2^n\, n!\sqrt{\pi}, \tag{169}$$

and satisfy the differential equation

$$\left[\frac{d^2}{dx^2} - 2x\,\frac{d}{dx} + 2n\right] H_n(x) = 0. \tag{170}$$

Some useful properties are

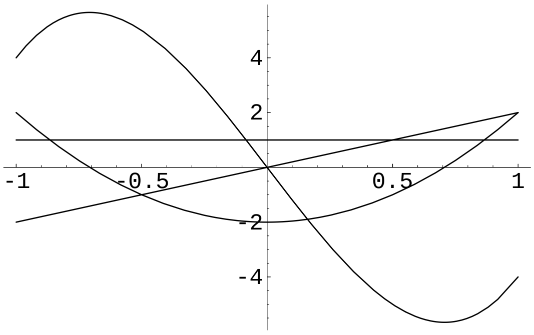
$$H_n(x) = (-)^n\, e^{x^2}\,\frac{d^n}{dx^n}\, e^{-x^2}, \tag{171}$$

$$x\, H_n(x) = \frac{1}{2}\, H_{n+1}(x) + n\, H_{n-1}(x), \tag{172}$$

$$\frac{d}{dx}\, H_n(x) = 2n\, H_{n-1}(x). \tag{173}$$

Some explicit polynomials are

$$\begin{aligned} H_0(x) &= 1, \\ H_1(x) &= 2x, \\ H_2(x) &= 4x^2 - 2, \\ H_3(x) &= 8x^3 - 12x. \end{aligned}$$



Plots of the $H_n(x)$ or `HermiteH[n,x]` functions for n = 0, 1, 2, and 3.

6.3 Three-dimensional harmonic oscillator

Because in the hamiltonian

$$H = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + \frac{1}{2}\, m\omega^2\, r^2, \tag{174}$$

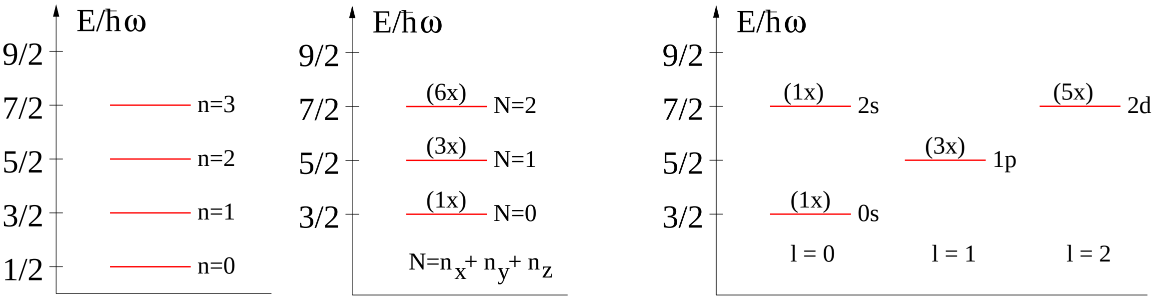
now both the kinetic term and the potential are separable, one sees that the hamiltonian of the 3-dimensional oscillator is the sum of three 1-dimensional oscillators. Thus the solution is given by

$$\phi_{n_x n_y n_z}(\boldsymbol{r}) = \phi_{n_x}(x)\,\phi_{n_y}(y)\,\phi_{n_z}(z), \tag{175}$$

with energy

$$E_{n_x n_y n_z} = \left(n_x + n_y + n_z + \frac{3}{2}\right)\hbar\omega. \tag{176}$$

The labels are integers and simple combinatorics show that a particular energy with $N = n_x + n_y + n_z$ is $\frac{1}{2}\,(N+1)(N+2)$-fold degerate.



The figures show the one-dimensional harmonic oscillator with energies $E = (n + 1/2)\hbar\omega$ (left), the degeneracy of the first three levels of the 3-dimensional harmonic oscillator (middle) and the assignment of orbital angular momentum (right).

Questions and exercises

1. For the harmonic oscillator one can also use the angular momentum quantum number ℓ. Why? Argue that for the three-dimensional harmonic oscillator the level $N = 1$ has $\ell = 1$. What are the possibilities for ℓ for the $N = 2$ levels.
2. How does one show what are the ℓ values for given N-levels for the three-dimensional harmonic oscillator.

Exercise 6.1

Give the eigenstates and eigenvalues of the 'half' oscillator with the potential

$$V(x) = \begin{cases} \infty & x < 0 \\ \frac{1}{2}m\omega^2 x^2 & x \geq 0 \end{cases} .$$

[Hint: use the results of the full oscillator.]

Exercise 6.2

The potential of the one-dimensional harmonic oscillator is given by

$$V(x) = \frac{1}{2}m\omega^2 x^2.$$

(a) Show that $H = p^2/(2m) + V(x)$ expressed in terms of $\xi = x\sqrt{\frac{m\omega}{\hbar}}$ is given by

$$H = \frac{1}{2}\hbar\omega\left[-\frac{d^2}{d\xi^2} + \xi^2\right]. \tag{177}$$

Define the operators

$$a = \frac{1}{\sqrt{2}}\left[\xi + \frac{\partial}{\partial\xi}\right] \quad \text{and} \quad a^\dagger = \frac{1}{\sqrt{2}}\left[\xi - \frac{\partial}{\partial\xi}\right].$$

(b) Determine the operators $a^\dagger a$ and $aa^\dagger$.
[Hint: use a test function (e.g. ϕ) to calculate $a^\dagger a\,\phi$.]

(c) Show that H can be written as

$$H = \hbar\omega\left[a^\dagger a + 1/2\right] = \hbar\omega\left[a a^\dagger - 1/2\right].$$

(d) Show that if $H\phi = E\phi$ (i.e. ϕ is a solution of the Schrödinger equation), it follows that

$$H(a^\dagger\phi) = (E + \hbar\omega)(a^\dagger\phi) \quad \text{and} \quad H(a\phi) = (E - \hbar\omega)(a\phi),$$

i.e. both $a\phi$ and $a^\dagger\phi$ are solutions of the Schrödinger equation as well, with shifted energies.
[Hint: use the expression for H under (c).]

(e) The solution with the lowest energy (ϕ_0) satisfies $a\phi_0 = 0$. Show that

$$\phi_0(\xi) = N e^{-\xi^2/2}.$$

(f) Determine the energy of the (ground) state ϕ_0.

(g) Give the general solution ϕ_n (up to a constant; don't worry about the normalization) and give the corresponding energy E_n.
[Hint: use the (creation) operator $a^\dagger$.]

7 Momentum operator and plane waves

7.1 Plane waves

Plane wave states are the eigenstates of the hermitean operator $\hat{\boldsymbol{p}}$

$$\hat{\boldsymbol{p}}\,\phi(\boldsymbol{r}) = -i\hbar\,\boldsymbol{\nabla}\phi(\boldsymbol{r}). \tag{178}$$

The eigenstates of the momentum operator are

$$\phi_k(\boldsymbol{r}) = \sqrt{\rho}\,\exp\left(i\,\boldsymbol{k}\cdot\boldsymbol{r}\right), \tag{179}$$

labeled by the vector $\boldsymbol{k}$, referred to as wave number. The actual eigenvalue is $\boldsymbol{p} = \hbar\boldsymbol{k}$. We have left ρ (interpreted as density) as an arbitrary normalization. Using the ket-notation one usually uses just $|\boldsymbol{k}\rangle$ rather than $|\phi_k\rangle$.

A convenient regularization is obtained by using box normalization, in which case one finds that for one particle in a box with sides L, i.e. $0 \le x \le L$, $0 \le y \le L$ and $0 \le z \le L$ (i.e. density $\rho = 1/L^3$), the wave function is found after imposing periodic boundary conditions[4],

$$\phi_k(\boldsymbol{r}) = \frac{1}{L^{3/2}}\,\exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}), \tag{180}$$

with $\boldsymbol{k} = (2\pi/L)\,(n_x, n_y, n_z)$, showing a density of states in k-space given by $(L/2\pi)^3$, which for instance means that 'counting' goes like

$$\sum_{(n_x,n_y,n_z)} = \left(\frac{L}{2\pi}\right)^3 \sum_{(k_x,k_y,k_z)} \longrightarrow \int \frac{d^3k}{(2\pi)^3\,\rho} = \int \frac{d^3p}{(2\pi\,\hbar)^3\,\rho}. \tag{181}$$

We have the following orthogonality properties for plane waves (given in discrete and in continuous form):

$$\langle\boldsymbol{k}|\boldsymbol{k}'\rangle = \delta_{n,n'} \;\longrightarrow\; \langle\boldsymbol{k}|\boldsymbol{k}'\rangle = \int d^3r\;\phi_k^*(\boldsymbol{r})\,\phi_{k'}(\boldsymbol{r}) = \rho\,(2\pi)^3\,\delta^3(\boldsymbol{k}-\boldsymbol{k}'). \tag{182}$$

The plane waves form a complete set of states, hence we know that

$$\phi(\boldsymbol{r}) = \sum_k \phi_k(\boldsymbol{r})\,c_k = \int \frac{d^3k}{(2\pi)^3\,\rho}\,\sqrt{\rho}\,\exp(i\,\boldsymbol{k}\cdot\boldsymbol{r})\,\tilde{\phi}(\boldsymbol{k}), \tag{183}$$

where

$$\tilde{\phi}(\boldsymbol{k}) = \int d^3r\,\sqrt{\rho}\,\exp(-i\,\boldsymbol{k}\cdot\boldsymbol{r})\,\phi(\boldsymbol{r}) \tag{184}$$

The quantity $\tilde{\phi}(k)$ is the Fourier transform of $\phi(\boldsymbol{r})$.

Common choices for the normalization of plane waves are $\rho = 1$ or $\rho = (2\pi)^{-3}$ (non-relativistic) and $\rho = E/M$ or $\rho = 2E$ (relativistic).

7.2 Flux associated with plane waves

The flux is obtained from the wave function via the expression for the current,

$$\boldsymbol{j}(\boldsymbol{r},t) = \frac{\hbar}{2i\,m}\left(\phi^*\,\boldsymbol{\nabla}\phi - (\boldsymbol{\nabla}\phi)^*\phi\right) = \rho\,\frac{\boldsymbol{p}}{m} = \rho\,\boldsymbol{v}. \tag{185}$$

The flux corresponding to a plane wave thus is along $\boldsymbol{p}$ and its magnitude is $\rho\,v$ (Exercise 2.3).

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[4] Periodic boundary conditions must be imposed to avoid getting an overcomplete set of states. For instance, hermiticity of the momentum operator requires that $\phi^*\phi|_0^L = 0$

7.3 Appendix: Dirac delta function

The Dirac delta-function is in fact a *distribution* (mapping functions into numbers), defined via

$$\int dx\; f(x)\,\delta(x) = f(0), \tag{186}$$

or $\int dx\; f(x)\,\delta(x-a) = f(a)$. It can be considered as the limit of a peaked function, e.g.

$$\delta(x) = \lim_{\epsilon\to 0} \phi_\epsilon(x), \tag{187}$$

where $\phi_\epsilon(x) = 0$ if $|x| > \epsilon/2$ and $\phi_\epsilon(x) = \epsilon$ if $|x| \le \epsilon/2$. Other examples are

$$\begin{aligned} \delta(x) &= \lim_{\Lambda\to\infty} \frac{\Lambda}{\sqrt{\pi}}\, e^{-\Lambda^2 x^2}, && (188)\\ \delta(x) &= \lim_{\Lambda\to\infty} \frac{\sin \Lambda x}{\pi\, x} = \lim_{\Lambda\to\infty} \int_{-\Lambda}^{\Lambda} \frac{dk}{2\pi}\, e^{i\,kx} && (189) \end{aligned}$$

Some properties are

$$\begin{aligned} &\delta(-x) = \delta(x),\\ &\delta(ax) = \frac{1}{|a|}\,\delta(x),\\ &x\,\delta(x) = 0,\\ &\int dx\; f(x)\,\delta(x-a) = f(a),\\ &\frac{d}{dx}\,\theta(x) = \delta(x), \end{aligned}$$

where $\theta(x)$ is the Heaviside function, $\theta(x) = 0$ for $x < 0$ and $\theta(x) = 1$ for $x \ge 0$. Note that Mathematica can work with this function, e.g. to define a square well potential with depth $-V_0$ using the expression $V(x) = -V_0\,\theta(\frac{1}{2}a + x)\,\theta(\frac{1}{2}a - x)$.

7.4 Wave packets

Suppose that we want to know what happens with a system that has a particular wave function $\psi(\boldsymbol{r}, 0) = \phi(\boldsymbol{r})$ at time zero, at which all interactions are switched off. The solutions of the hamiltonian in case of absence of any interaction ($V = 0$), are the plane waves (momentum eigenstates). Thus what one has to do is determine the amplitudes of the plane waves, which means calculating $\tilde\phi(\boldsymbol{k})$ and then one simply multiply them by the time-dependent plane wave solutions. So given the above boundary condition one has after switching off interactions

$$\psi(\boldsymbol{r}, t) = \int \frac{d^3k}{(2\pi)^3}\; \tilde\phi(k)\, exp(i\,\boldsymbol{k}\cdot\boldsymbol{r} - i\,\omega_k t) \tag{190}$$

with $\omega_k = \hbar k^2/2m$ (We take $\rho = 1$). The absolute value squared $|\tilde\phi(\boldsymbol{k})|^2/(2\pi\hbar)^3$ is the probability of the outcome of a momentum measurement with outcome $\boldsymbol{p} = \hbar\boldsymbol{k}$.

Next, we give some examples of calculations of the Fourier transform. Starting with a one-dimensional example, the harmonic oscillator one has (we take $\rho = 1$)

$$\phi(x) = \left(\frac{\alpha^2}{\pi}\right)^{1/4} \exp\left(-\frac{1}{2}\,\alpha^2 x^2\right) \quad\Longleftrightarrow\quad \tilde\phi(k) = \left(\frac{1}{\pi\alpha^2}\right)^{1/4} \exp\left(-\frac{1}{2}\,\frac{k^2}{\alpha^2}\right), \tag{191}$$

with $\alpha = \sqrt{m\omega/\hbar}$. The calculation (omitting first the normalization) proceeds via

$$\begin{aligned}\tilde{\phi}(k) &\propto \int dx\; e^{-i\,kx}\, \exp\left(-\frac{1}{2}\,\alpha^2 x^2\right) \\ &\propto \int dx\; \exp\left(-\frac{1}{2}\,\alpha^2\left(x + 2i\,\frac{k}{\alpha^2}\right)^2 - \frac{1}{2}\,\frac{k^2}{\alpha^2}\right) \;\propto\; \exp\left(-\frac{1}{2}\,\frac{k^2}{\alpha^2}\right),\end{aligned}$$

As a three-dimensional example we have

$$\phi(\boldsymbol{r}) = \sqrt{\frac{\mu}{2\pi}}\,\frac{e^{-\mu r}}{r} \qquad \Longleftrightarrow \qquad \tilde{\phi}(\boldsymbol{k}) = \frac{\sqrt{8\pi\,\mu}}{\boldsymbol{k}^2 + \mu^2} = \sqrt{\frac{8\pi}{\mu^3}}\,\frac{1}{(1 + k^2/\mu^2)}. \tag{192}$$

Omitting the normalization factor the Fourier transform is found as follows

$$\begin{aligned}\tilde{\phi}(\boldsymbol{k}) &\propto \int d^3r\; \exp(-i\,\boldsymbol{k}\cdot\boldsymbol{r})\,\frac{e^{-\mu r}}{r} = 2\pi\int_0^\infty r^2\,dr \int_{-1}^{1} dX\; e^{i\,kr\,X}\,\frac{e^{-\mu r}}{r} \\ &= \frac{2\pi}{i\,k}\int_0^\infty dr\;\left(e^{(i\,k-\mu)r} - e^{(-i\,k-\mu)r}\right) = \frac{2\pi}{i\,k}\left(\frac{1}{i\,k-\mu} - \frac{1}{-i\,k-\mu}\right) = \frac{4\pi}{k^2+\mu^2}.\end{aligned} \tag{193}$$

The result for the normalized wave function in $\boldsymbol{k}$-space is found after multiplying with the normalization factor.

Exercises

Exercise 7.1

(a) Show that the operator $p_x = -i\hbar\, d/dx$ is hermitean, i.e.

$$\int_{-\infty}^{\infty} dx\; \phi^*(x)\left(-i\hbar\,\frac{d}{dx}\phi\right) = \int_{-\infty}^{\infty} dx\;\left(i\hbar\,\frac{d}{dx}\phi^*\right)\phi(x).$$

(b) Show that for wave functions in a box ($0 \le x \le L$) one must impose boundary conditions on the wave functions to assure that p_x is hermitean. Show that $\phi(0) = \pm\phi(L)$ are sufficient conditions.

Exercise 7.2

Use the result of section 7.4,

$$\phi(\boldsymbol{r}) = \frac{e^{-\mu r}}{r} \qquad \Rightarrow \qquad \tilde{\phi}(\boldsymbol{k}) = \frac{4\pi}{\boldsymbol{k}^2 + \mu^2}.$$

to find the Fourier transform $\tilde{\phi}(\boldsymbol{k})$ for the Hydrogen ground state wave function,

$$\phi(\boldsymbol{r}) = \left(\frac{1}{\pi\,a_0^3}\right)^{1/2} e^{-r/a_0}.$$

[Hint: Use that $e^{-\mu r} = -\frac{d}{d\mu}\,(e^{-\mu r}/r)$.]

8 Dirac notation

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

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

$$\left.\begin{array}{l} |u_1\rangle \in \mathscr{H} \\ |u_2\rangle \in \mathscr{H} \\ c_1, c_2 \in \mathbb{C} \end{array}\right\} \longrightarrow c_1|u_1\rangle + c_2|u_2\rangle \in \mathscr{H} \tag{194}$$

- 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*),

$$|u\rangle \in \mathscr{H} \longrightarrow |u\rangle = \sum_{n=1}^{N} c_n |u_n\rangle. \tag{195}$$

8.2 Scalar product and the (dual) bra-space

For elements $|u\rangle$, $|v\rangle \in \mathscr{H}$ we can construct the complex number $\langle u|v\rangle \in \mathbb{C}$, 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, $\mathscr{H}^* = \{\langle u|\}$, which is anti-linear meaning that

$$|u\rangle = c_1|u_1\rangle + c_2|u_2\rangle \longleftrightarrow \langle u| = c_1^*\langle u_1| + c_2^*\langle u_2|. \tag{196}$$

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

8.3 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

$$|u\rangle = \sum_n |u_n\rangle \underbrace{\langle u_n|u\rangle}_{c_n} = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}. \tag{197}$$

- Note that

$$\langle u|u\rangle = 1 \;\longleftrightarrow\; \sum_n |c_n|^2 = 1, \tag{198}$$

  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.

8.4 Operators

- An operator A acts in the Hilbert-space $\mathscr{H}$, i.e. $|v\rangle = A|u\rangle = |Au\rangle \in \mathscr{H}$.
- 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
  $$I = \sum_n |u_n\rangle\langle u_n|, \tag{199}$$
  directly following from Eq. 197 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 $A|u\rangle$
  $$\begin{aligned} A|u\rangle &= \sum_n A|u_n\rangle\langle u_n|u\rangle \\ &= \sum_{m,n} |u_m\rangle \underbrace{\langle u_m|A|u_n\rangle}_{A_{mn}} \underbrace{\langle u_n|u\rangle}_{c_n} = \sum_m |u_m\rangle \left(\sum_n A_{mn}c_n\right) \\ &= \begin{pmatrix} A_{11} & A_{12} & \dots \\ A_{21} & A_{22} & \dots \\ \vdots & \vdots & \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} \end{aligned} \tag{200}$$
  and the matrix element of A is given by
  $$\begin{aligned} \langle u|A|u\rangle &= \sum_{m,n} \underbrace{\langle u|u_m\rangle}_{c_m^*} \underbrace{\langle u_m|A|u_n\rangle}_{A_{mn}} \underbrace{\langle u_n|u\rangle}_{c_n} \\ &= (c_1^*\ c_2^*\ \dots) \begin{pmatrix} A_{11} & A_{12} & \dots \\ A_{21} & A_{22} & \dots \\ \vdots & \vdots & \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} \end{aligned} \tag{201}$$

8.5 Adjoint operator

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

$$\langle u|A^\dagger|v\rangle \equiv \langle v|A|u\rangle^*. \tag{202}$$

We note that de bra-state $\langle Au| = \langle u|A^\dagger$. This is proven in the following way: for every $|v\rangle$ is $\langle Au|v\rangle = \langle v|Au\rangle^* = \langle v|A|u\rangle^* = \langle u|A^\dagger|v\rangle$. In matrix language one this has that $A^\dagger = A^{T*}$.

8.6 Hermitean operators

- Definition: An operator A is hermitean when $\langle u|Au\rangle = \langle Au|u\rangle$. By applying this to 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

$$\langle u|A|v\rangle = \langle u|A^\dagger|v\rangle = \langle v|A|u\rangle^* \tag{203}$$

$$\langle u|A|u\rangle = \langle u|A|u\rangle^* \quad \rightarrow \quad \text{real expectation values} \tag{204}$$

- For the eigenvalues (a_n) and eigenstates ($|n\rangle$), of a hermitean operator, $A|n\rangle = a_n|n\rangle$ we have
  - $\langle n|A|n\rangle = a_n$ 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). Eigenstates can be normalized, $\langle n|n\rangle = 1$.
  - Thus, eigenstates form an orthonormal basis, $\langle m|n\rangle = \delta_{mn}$. Using this basis A is diagonal,

$$A = \sum_n |n\rangle a_n \langle n| = \begin{pmatrix} a_1 & 0 & \dots \\ 0 & a_2 & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \tag{205}$$

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

$$\langle u|A|u\rangle = \sum_n \underbrace{\langle u|n\rangle}_{c_n^*} a_n \underbrace{\langle n|u\rangle}_{c_n} = \sum_n a_n\,|c_n|^2. \tag{206}$$

  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.

8.7 Unitary operators

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

$$\langle Uv|Uw\rangle = \langle v|w\rangle \tag{207}$$

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

Exercises

Exercise 8.1

In many applications we will encounter the Pauli matrices being (hermitean) operators in the 2-dimensional space of complex spinors,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Find the eigenvalues and eigenvectors of these operators.

Exercise 8.2

Using the definition of adjoint operator, show that a unitary operator conserves scalar products (Eq. 207)

9 Representations of states

9.1 Coordinate-representation

With the Dirac notation at hand, we can formalize some issues on wave mechanics. We have used $|\psi\rangle$ and $\psi(\boldsymbol{r})$ more or less interchangeable. To formalize we simply write down the eigenvalue equation for the hermitean operator operator $\hat{\boldsymbol{r}}$, denoting the eigenstates as $|\boldsymbol{r}\rangle$ and the eigenvalues as $\boldsymbol{r}$. Thus

$$\hat{\boldsymbol{r}}|\boldsymbol{r}\rangle = \boldsymbol{r}|\boldsymbol{r}\rangle, \tag{208}$$

We have the following properties:

(i) Orthogonality: $\langle\boldsymbol{r}|\boldsymbol{r}'\rangle = \delta^3(\boldsymbol{r}-\boldsymbol{r}')$ (See section 7.3 for the definition)

(ii) The value $\psi(\boldsymbol{r}) \in \mathbb{C}$ is simply the coefficient in the expansion $|\psi\rangle = \displaystyle\int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle \underbrace{\langle\boldsymbol{r}|\psi\rangle}_{\psi(\boldsymbol{r})}$.

(iii) The identity: $I = \displaystyle\int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle\langle\boldsymbol{r}|$

(iv) The operator expansion: $\hat{\boldsymbol{r}} = \displaystyle\int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle\boldsymbol{r}\langle\boldsymbol{r}|$

We of course should check that the above is consistent and agrees with the wave formulation of quantum mechanics. The most important check is to calculate the behavior of the function $\hat{\boldsymbol{r}}\psi$. Using property (ii) and the definition 208 in the form $\langle\boldsymbol{r}|\hat{\boldsymbol{r}} = \boldsymbol{r}\langle\boldsymbol{r}|$ (hermiticity) we get

$$\hat{\boldsymbol{r}}\psi(\boldsymbol{r}) = \langle\boldsymbol{r}|\hat{\boldsymbol{r}}|\psi\rangle = \boldsymbol{r}\,\langle\boldsymbol{r}|\psi\rangle = \boldsymbol{r}\,\psi(\boldsymbol{r}),$$

so indeed the operator does what we already saw before. We can check other consistency requirements,

- 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 of two states: $\langle\psi|\phi\rangle = \int d^3\boldsymbol{r}\ \underbrace{\langle\psi|\boldsymbol{r}\rangle}_{\psi^*(\boldsymbol{r})}\underbrace{\langle\boldsymbol{r}|\phi\rangle}_{\phi(\boldsymbol{r})} = \int d^3\boldsymbol{r}\ \psi^*(\boldsymbol{r})\phi(\boldsymbol{r})$
- Expectation value: $\langle\psi|\hat{\boldsymbol{r}}|\psi\rangle = \int d^3\boldsymbol{r}\ \langle\psi|\boldsymbol{r}\rangle\boldsymbol{r}\langle\boldsymbol{r}|\psi\rangle = \int d^3\boldsymbol{r}\ \boldsymbol{r}\,|\psi(\boldsymbol{r})|^2$

Knowing that $V(\hat{\boldsymbol{r}})\psi(\boldsymbol{r}) = V(\boldsymbol{r})\psi(\boldsymbol{r})$ and $\hat{\boldsymbol{p}}\psi(\boldsymbol{r}) = -i\hbar\boldsymbol{\nabla}\psi(\boldsymbol{r})$ we have among others

$$V(\hat{\boldsymbol{r}}) = \int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle V(\boldsymbol{r})\langle\boldsymbol{r}|, \tag{209}$$

$$\hat{\boldsymbol{p}} = \int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle\,(-i\hbar\boldsymbol{\nabla})\,\langle\boldsymbol{r}|. \tag{210}$$

9.2 Momentum-representation

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

$$\hat{\boldsymbol{p}}|\boldsymbol{p}\rangle = \boldsymbol{p}|\boldsymbol{p}\rangle. \tag{211}$$

We already have seen that in the coordinate representation for $|\boldsymbol{p}\rangle$:

$$\hat{\boldsymbol{p}}\phi_p(\boldsymbol{r}) = \boldsymbol{p}\phi_p(\boldsymbol{r}) \ \longrightarrow\ \underbrace{\phi_p(\boldsymbol{r})}_{\langle\boldsymbol{r}|\boldsymbol{p}\rangle} = \sqrt{\rho}\,\exp\left(\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right) \tag{212}$$

(This defines ρ). We then 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 is achieved via,

$$\psi(\boldsymbol{r}) = \langle \boldsymbol{r}|\psi\rangle = \int \frac{d^3\boldsymbol{p}}{(2\pi\hbar)^3\,\rho}\;\langle \boldsymbol{r}|\boldsymbol{p}\rangle\langle \boldsymbol{p}|\psi\rangle = \int \frac{d^3\boldsymbol{p}}{(2\pi\hbar)^3\,\rho}\;\sqrt{\rho}\,\exp\left(\frac{i}{\hbar}\,\boldsymbol{p}\cdot\boldsymbol{r}\right)\tilde{\psi}(\boldsymbol{p}), \tag{213}$$

$$\tilde{\psi}(\boldsymbol{p}) = \langle \boldsymbol{p}|\psi\rangle = \int d^3\boldsymbol{r}\;\langle \boldsymbol{p}|\boldsymbol{r}\rangle\langle \boldsymbol{r}|\psi\rangle = \int d^3\boldsymbol{r}\;\sqrt{\rho}\;\exp\left(-\frac{i}{\hbar}\,\boldsymbol{p}\cdot\boldsymbol{r}\right)\psi(\boldsymbol{r}), \tag{214}$$

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

For instance consistency of Eq. 212 and (iv) can be checked,

$$\begin{aligned}\langle \boldsymbol{r}|\hat{\boldsymbol{p}}|\psi\rangle &= \int \frac{d^3\boldsymbol{p}}{(2\pi\hbar)^3\,\rho}\;\langle \boldsymbol{r}|\boldsymbol{p}\rangle\boldsymbol{p}\langle \boldsymbol{p}|\psi\rangle = \int \frac{d^3\boldsymbol{p}}{(2\pi\hbar)^3\,\rho}\;\boldsymbol{p}\,\sqrt{\rho}\,\exp\left(\frac{i}{\hbar}\,\boldsymbol{p}\cdot\boldsymbol{r}\right)\tilde{\psi}(\boldsymbol{p})\\ &= -i\hbar\boldsymbol{\nabla}\int \frac{d^3\boldsymbol{p}}{(2\pi\hbar)^3\,\rho}\;\sqrt{\rho}\,\exp\left(\frac{i}{\hbar}\,\boldsymbol{p}\cdot\boldsymbol{r}\right)\tilde{\psi}(\boldsymbol{p}) = -i\hbar\boldsymbol{\nabla}\psi(\boldsymbol{r})\end{aligned} \tag{215}$$

and finally we note that the expectation value of the momentum squared can be calculated from $\psi(\boldsymbol{r})$ or from $\tilde{\psi}(\boldsymbol{k})$,

$$\langle \boldsymbol{p}^2\rangle = \int d^3r\;\psi^*(\boldsymbol{r})\left(-\hbar^2\boldsymbol{\nabla}^2\right)\psi(\boldsymbol{r}) = \int \frac{d^3k}{(2\pi)^3\,\rho}\;\hbar^2\boldsymbol{k}^2\,|\tilde{\psi}(\boldsymbol{k})|^2. \tag{216}$$

Exercises

Exercise 9.1

Use the momentum wave function of the Hydrogen atom (outcome of Exercise 7.2),

$$\tilde{\phi}(\boldsymbol{k}) = 8\,\pi^{1/2}\,a_0^{3/2}\,\frac{1}{(1+k^2\,a_0^2)^2}.$$

to find $\langle \boldsymbol{p}^2\rangle$ for the Hydrogen ground state.
Useful definite integrals are

$$\int_0^\infty \frac{x^2\,dx}{(1+x^2)^4} = \int_0^\infty \frac{x^4\,dx}{(1+x^2)^4} = \frac{\pi}{32}$$

Exercise 9.2

Show that $\langle \boldsymbol{p}|\hat{\boldsymbol{r}}\psi\rangle = i\hbar\boldsymbol{\nabla}_p\tilde{\psi}(\boldsymbol{p})$, which implies that in momentum representation

$$\hat{\boldsymbol{r}} = \int \frac{d^3p}{(2\pi\hbar)^3}\;|\boldsymbol{p}\rangle(i\hbar\boldsymbol{\nabla}_p)\langle \boldsymbol{p}|.$$

10 Several observables and commutation relations

10.1 Compatibility of observables

Consider well-known observables like $\boldsymbol{r}$, $\boldsymbol{p}$ or $\boldsymbol{\ell} = \boldsymbol{r} \times \boldsymbol{p}$. Classically these are (possibly time-dependent) properties of a system. Quantummechanically they are operators that constitute "abstract" measuring devices, with a spectrum of possible outcomes as we have seen in the Stern-Gerlach experiment.

We will now consider what happens when several measurements are performed, one after the other. We denote this as

$$\text{state} \to \boxed{\text{measurement}} \to \text{eigenvalue} \to \text{state}.$$

As an example take a particle with $\ell_z = \hbar$ described by a wave function of the form $\sim (x + i\,y)\,f(r)/\sqrt{2}$. We have schematically after measurements of ℓ_z followed by a measurement of ℓ_x:

$$\frac{x+i\,y}{\sqrt{2}} \to \boxed{\hat{\ell}_z} \to \begin{cases} \ell_z = 1 & 100\% \quad \to \frac{x+i\,y}{\sqrt{2}} \to \boxed{\hat{\ell}_x} \to \begin{cases} \ell_x = 1 & 25\% & \to (y+i\,z)/\sqrt{2} \\ \ell_x = 0 & 50\% & \to x \\ \ell_x = -1 & 25\% & \to (y-i\,z)/\sqrt{2} \end{cases} \\ \ell_z = 0 & 0\% \\ \ell_z = -1 & 0\% \end{cases}$$

while in the other order one gets

$$\frac{x+i\,y}{\sqrt{2}} \to \boxed{\hat{\ell}_x} \to \begin{cases} \ell_x = 1 & 25\% \quad \to \frac{y+i\,z}{\sqrt{2}} \quad \to \boxed{\hat{\ell}_z} \to \begin{cases} \ell_z = 1 & 25\% & \to (x+i\,y)/\sqrt{2} \\ \ell_z = 0 & 50\% & \to z \\ \ell_z = -1 & 25\% & \to (x-i\,y)/\sqrt{2} \end{cases} \\ \ell_x = 0 & 50\% \quad \to x \quad \to \boxed{\hat{\ell}_z} \to \begin{cases} \ell_z = 1 & 50\% & \to (x+i\,y)/\sqrt{2} \\ \ell_z = 0 & 0\% & \to z \\ \ell_z = -1 & 50\% & \to (x-i\,y)/\sqrt{2} \end{cases} \\ \ell_x = -1 & 25\% \quad \to \frac{y-i\,z}{\sqrt{2}} \quad \to \boxed{\hat{\ell}_z} \to \begin{cases} \ell_z = 1 & 25\% & \to (x+i\,y)/\sqrt{2} \\ \ell_z = 0 & 50\% & \to z \\ \ell_z = -1 & 25\% & \to (x-i\,y)/\sqrt{2} \end{cases} \end{cases}$$

The resulting distributions after the measurements thus are:

measurements		probabilities		measurements		probabilities	
ℓ_z	ℓ_x	quantum	classical	ℓ_x	ℓ_z	quantum	classical
1	1	1/4	0	1	1	1/16	0
1	0	1/2	1	0	1	1/4	1
1	-1	1/4	0	-1	1	1/16	0
0	1	0	0	1	0	1/8	0
0	0	0	0	0	0	0	0
0	-1	0	0	-1	0	1/8	0
-1	1	0	0	1	-1	1/16	0
-1	0	0	0	0	-1	1/4	0
-1	-1	0	0	-1	-1	1/16	0

The conclusion is that the order of measuremements matters for ℓ_x and ℓ_z. Such measurements are called noncompatible. If one does the same with measurements of momentum one finds that the order doesn't matter:

$$\exp(i\,\boldsymbol{p}\cdot\boldsymbol{r}/\hbar) \to \boxed{\hat{p}_x} \to p_x \to \exp(i\,\boldsymbol{p}\cdot\boldsymbol{r}/\hbar) \to \boxed{\hat{p}_y} \to p_y \to \exp(i\,\boldsymbol{p}\cdot\boldsymbol{r}/\hbar)$$

$$\exp(i\,\boldsymbol{p}\cdot\boldsymbol{r}/\hbar) \to \boxed{\hat{p}_y} \to p_y \to \exp(i\,\boldsymbol{p}\cdot\boldsymbol{r}/\hbar) \to \boxed{\hat{p}_x} \to p_x \to \exp(i\,\boldsymbol{p}\cdot\boldsymbol{r}/\hbar)$$

The measurements are compatible.

10.2 Compatibility of operators and commutators

Definition: Two operators A and B are compatible if they have a common (complete) orthonormal set of eigenfunctions.

For compatible operators we know after a measurement of A followed by a measurement of B both eigenvalues and we can confirm this by performing again a measurement of A. Suppose we have a complete common set ψ_{abk}, labeled by the eigenvalues of A, B and possibly an index k in case of degeneracy. Thus $A\,\psi_{abk} = a\,\psi_{abk}$ and $B\,\psi_{abk} = b\,\psi_{abk}$. Suppose we have an arbitrary state $\psi = \sum_{abk} c_{abk}\,\psi_{abk}$, then we see that measurements of A and B or those in reverse order yield similar results,

$$\psi \rightarrow \boxed{\text{A}} \rightarrow a \rightarrow \sum_{b,k} c_{abk}\,\psi_{abk} \rightarrow \boxed{\text{B}} \rightarrow b \rightarrow \sum_{k} c_{abk}\,\psi_{abk},$$
$$\psi \rightarrow \boxed{\text{B}} \rightarrow b \rightarrow \sum_{a,k} c_{abk}\,\psi_{abk} \rightarrow \boxed{\text{A}} \rightarrow a \rightarrow \sum_{k} c_{abk}\,\psi_{abk}.$$

Next consider the property of *commutativity.*

Definition: The commutator of two operators is defined as $[A,B] = AB - BA$.
Properties: $[A,B] = -[B,A]$
$[A,B+C] = [A,B] + [A,C]$ (linear),
$[A,BC] = [A,B]C + B[A,C]$,
$[A,[B,C]] + [B,[C,A]] + [C,[A,B]] = 0$ (Jacobi identity),
$[f(A),A] = 0$.

These properties are simple to prove, e.g. $[A,BC] \equiv ABC - BCA = ABC - BAC + BAC - BCA = [A,B]C - B[A,C]$. The last property follows because a function of operators is defined via a Taylor expansion in terms of powers of A, $f(A) = c_0\,1 + c_1\,A + c_2\,A^2 + \ldots$ and the fact that $[A^n,A] = A^n A - A A^n = 0$.

The most important nonvanishing commutator is the one between position and momentum,

$$[r_i, r_j] = 0, \tag{217}$$
$$[p_i, p_j] = 0, \tag{218}$$
$$[r_i, p_j] = i\hbar\,\delta_{ij}. \tag{219}$$

Let us proof the important relation Eq. 219. We have

$$\begin{aligned} \hat{x}\,\hat{p}_x\,\psi(x) &= \hat{x}\left(-i\hbar\,\frac{\partial}{\partial x}\,\psi\right) = -i\hbar\,x\,\frac{\partial}{\partial x}\,\psi \\ \hat{p}_x\,\hat{x}\,\psi(x) &= -i\hbar\,\frac{\partial}{\partial x}\,(x\,\psi) = -i\hbar\,x\,\frac{\partial}{\partial x}\,\psi - i\hbar\,\psi \end{aligned}$$

Thus the difference is

$$[\hat{x},\hat{p}_x]\,\psi(x) = (\hat{x}\,\hat{p}_x - \hat{p}_x\,\hat{x})\,\psi(x) = i\hbar\,\psi(x).$$

This is valid for any function ψ, thus $[\hat{x}, \hat{p}_x] = 1$. Other examples of commutators[5] are

$$[\ell_i, \ell_j] = i\hbar\, \epsilon_{ijk}\, \ell_k, \tag{220}$$

$$[\boldsymbol{\ell}^2, \ell_i] = 0, \tag{221}$$

$$[\ell_i, r_j] = i\hbar\, \epsilon_{ijk}\, r_k, \tag{222}$$

$$[\ell_i, p_j] = i\hbar\, \epsilon_{ijk}\, p_k, \tag{223}$$

$$[\ell_i, \boldsymbol{r}^2] = 0, \tag{224}$$

$$[\ell_i, \boldsymbol{p}^2] = 0, \tag{225}$$

$$[\ell_i, \boldsymbol{p}\cdot\boldsymbol{r}] = 0, \tag{226}$$

$$[p_i, \boldsymbol{r}^2] = -2\, i\hbar\, r_i, \tag{227}$$

$$[r_i, \boldsymbol{p}^2] = 2\, i\hbar\, p_i, \tag{228}$$

$$[p_i, V(\boldsymbol{r})] = -i\hbar\, \nabla_i V. \tag{229}$$

Above we have given a proof using the explicit definitions of the operators. One can also use the properties, e.g. to proof Eq. 226. One has $[\ell_z, xp_x] = [\ell_z, x]p_x + x[\ell_z, p_x] = i\hbar(yp_x + xp_y)$, $[\ell_z, yp_y] = i\hbar(-xp_x - yp_y)$, and $[\ell_z, zp_z] = 0$ using the third of the properties given above. The linearity then gives the result.
The following theorem connects commutativity and compatibility:

Theorem: A and B are compatible $\Longleftrightarrow$ $[A, B] = 0$

> *Proof ($\Rightarrow$): There exists a complete common set ψ_n of eigenfunctions for which one thus has $[A, B]\psi_n = (AB - BA)\psi_n = (a_n b_n - b_n a_n)\psi_n = 0$.*
> *Proof ($\Leftarrow$): Suppose ψ_a eigenfunction of A. Then $A(B\psi_a) = AB\psi_a = BA\psi_a = B\, a\psi_a = a\, B\psi_a$. Thus $B\psi_a$ is also an eigenfunction of A. Then one can distinguish*
> *(i) If a is nondegenerate, then $B\psi_a \propto \psi_a$, say $B\psi_a = b\psi_a$ which implies that ψ_a is also an eigenfunction of B.*
> *(ii) If a is degenerate (degeneracy s), consider that part of the Hilbert space that is spanned by the functions ψ_{ar} ($r = 1, \ldots, s$). For a given ψ_{ap} (eigenfunction of A) $B\psi_{ap}$ also can be written in terms of the ψ_{ar}. Thus we have an hermitean operator B in the subspace of the functions ψ_{ar}. In this subspace B can be diagonalized, and we can use the eigenvalues $b_1, \ldots b_s$ as second label, which leads to a common set of eigenfunctions.*

We have seen the case of degeneracy for the spherical harmonics. The operators $\boldsymbol{\ell}^2$ and ℓ_z commute and the Y^ℓ_m are the common set of eigenfunctions.

10.3 Constants of motion

Definition: A hermitean operator A is a constant of motion if
(i) A is compatible with the Hamiltonian, i.e. $[A, H] = 0$.
(ii) A does not have explicit time dependence, i.e. $\frac{\partial A}{\partial t} = 0$, e.g. $A = A(\boldsymbol{r}, \boldsymbol{p}, \boldsymbol{\ell})$.

Examples of constants of motion, compatible with the hamiltonian and thus providing eigenvalues that can be used to label eigenfunctions, are:

- The hamiltonian for a free particle:

$$H = \frac{p^2}{2M} \qquad \text{Compatible set:} \quad H, \boldsymbol{p}$$

The plane waves $u_k(\boldsymbol{r}) = \exp(i\, \boldsymbol{k}\cdot\boldsymbol{r})$ form a common set of eigenfunctions.

---

[5] The Levi-Civita tensor $\epsilon_{ijk} = 0$ if any two indices are equal, while $\epsilon_{ijk} = \pm 1$ if ijk is an even/odd permutation of 123.

- The hamiltonian with a central potential:

$$H = \frac{p^2}{2M} + V(|\boldsymbol{r}|) \qquad \text{Compatible set:} \quad H, \boldsymbol{\ell}^2, \ell_z$$

  This allows writing the eigenfunctions of this hamiltonian as $\psi_{n\ell m} = (u(r)/r)\, Y_m^\ell(\theta, \varphi)$.

- The hamiltonian with a potential depending only on z:

$$H = \frac{p^2}{2M} + V(z) \qquad \text{Compatible set:} \quad H, \ell_z \quad \text{or} \quad H, p_x, p_y$$

  This shows that eigenfunctions can be written as $\phi(z)\, \exp(i\, k_x x + i\, k_y y)$ or as $\phi(r,\theta)\, \exp(i\, m\varphi)$.

Theorem: A is a constant of motion $\Rightarrow \frac{d}{dt}\langle A\rangle = 0$.

Proof:

$$\begin{aligned} \frac{d}{dt}\langle A\rangle &= \frac{d}{dt}\int d^3r\ \psi^*(\boldsymbol{r},t) A \psi(\boldsymbol{r},t) = \int d^3r\ \left[\frac{\partial\psi^*}{\partial t}\, A\psi + \psi^*\, A\frac{\partial\psi}{\partial t} + \psi^*\, \frac{\partial A}{\partial t}\, \psi\right] \\ &= \int d^3r\ \left[\left(\frac{1}{i\hbar} H\psi\right)^* A\psi + \psi^*\, A\frac{1}{i\hbar}\, H\psi\right] = \frac{1}{i\hbar}\int d^3r\ \left[-\psi^*\, HA\,\psi + \psi^*\, AH\,\psi\right] = 0 \end{aligned}$$

Note that the general relation that is actual written down in this proof is

$$i\hbar\,\frac{d}{dt}\langle A\rangle = i\hbar\,\langle\frac{\partial}{\partial t}A\rangle + \langle[A,H]\rangle. \tag{230}$$

Examples of this relation are the Ehrenfest relations

$$\frac{d}{dt}\langle\boldsymbol{p}\rangle = \frac{1}{i\hbar}\langle[\boldsymbol{p},H]\rangle = \frac{1}{i\hbar}\langle[\boldsymbol{p},V(\boldsymbol{r})]\rangle = \langle-\boldsymbol{\nabla}V(\boldsymbol{r})\rangle, \tag{231}$$

$$\frac{d}{dt}\langle\boldsymbol{r}\rangle = \frac{1}{i\hbar}\langle[\boldsymbol{r},H]\rangle = \frac{1}{i\hbar}\,\frac{1}{2m}\langle[\boldsymbol{r},\boldsymbol{p}^2]\rangle = \frac{\langle\boldsymbol{p}\rangle}{m}. \tag{232}$$

Exercises

Exercise 10.1

(a) Calculate for the position and momentum operators, x, y and $p_y = -i\hbar\frac{\partial}{\partial y}$ the commutators

$$[y, p_y] \qquad \text{en} \qquad [x, p_y].$$

(b) Determine from the known commutation relations for $[r_i, p_j]$ (i and j are components of $\boldsymbol{r}$ and $\boldsymbol{p}$) the commutation relations for the angular momentum operators $\boldsymbol{\ell} = \boldsymbol{r}\times\boldsymbol{p}$,

$$[\ell_z, x], \quad [\ell_y, p_z], \quad [\ell_y, \ell_z].$$

Exercise 10.2

In this exercise we use

$$\langle\psi\,|A|\,\psi\rangle = \int \mathrm{d}^3\boldsymbol{r}\ \psi^*(\boldsymbol{r},t) A\psi(\boldsymbol{r},t)\ .$$

Given the hamiltonian

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

(a) Show that for an eigenstate $\psi_n(\boldsymbol{r},t)$ of H,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi_n\,|\boldsymbol{r}\cdot\boldsymbol{p}\,|\,\psi_n\rangle = 0.$$

(b) Derive from the commutation relations and with the help of the answer in (a) the virial theorem

$$\langle\psi_n\,|T|\,\psi_n\rangle = \frac{1}{2}\langle\psi_n\,|\boldsymbol{r}\cdot(\boldsymbol{\nabla}V(\boldsymbol{r}))|\,\psi_n\rangle$$

in which T is the operator for the kinetic energy part.

(c) Consider a 3-dimensional harmonic oscillator. Show that if the system is in an eigenstate of H that de expectation value of the kinetic energy equals the expectation value of the potential energy.

11 The uncertainty principle

11.1 The uncertainty relation for noncompatible observables

For measurements of observables A and B (operators) we have

$[A, B] = 0 \Rightarrow$ A and B have common set of eigenstates.
For these common eigenstates one has $\Delta A = \Delta B = 0$ and hence $\Delta A\,\Delta B = 0$.
$[A, B] \neq 0 \Rightarrow$ A and B are not simultaneously measurable.
One has $\Delta A\,\Delta B \geq \frac{1}{2}|\langle\,[A, B]\,\rangle|$, known as the *uncertainty relation.*

> *The proof of the uncertainty relation is in essence a triangle relation for inner products. Define for two hermitean operators A and B, the (also hermitean) operators $\alpha = A - \langle A\rangle$ and $\beta = B - \langle B\rangle$. We have $[\alpha, \beta] = [A, B]$. Using positivity for any state, in particular $|(\alpha + i\lambda\,\beta)\psi\rangle$ with λ arbitrary, one has*
>
> $$0 \leq \langle(\alpha + i\lambda\,\beta)\psi|(\alpha + i\lambda\,\beta)\psi\rangle = \langle\psi|(\alpha - i\lambda\,\beta)(\alpha + i\lambda\,\beta)|\psi\rangle = \langle\alpha^2\rangle + \lambda^2\,\langle\beta^2\rangle + \lambda\,\underbrace{\langle\,i[\alpha, \beta]\,\rangle}_{\langle\gamma\rangle}.$$
>
> *Since $i\,[\alpha, \beta]$ is a hermitean operator (Exercise 3.4, Mandl), $\langle\gamma\rangle$ is real. Positivity of the quadratic equation $\langle\alpha^2\rangle + \lambda^2\,\langle\beta^2\rangle + \lambda\,\langle\gamma\rangle \geq 0$ for all λ gives $4\,\langle\alpha^2\rangle\,\langle\beta^2\rangle \geq \langle\gamma\rangle^2$. Taking the square root then gives the desired result.*

The most well-known example of the uncertainty relation is the one originating from the noncompatibility of positionn and momentum operator, specifically from $[x, p_x] = i\hbar$ one gets

$$\Delta x\,\Delta p_x \geq \frac{1}{2}\,\hbar. \tag{233}$$

An example is the Gaussian wave packet that we saw before,

$$\psi(x) = N\,\exp\left(-\frac{1}{2}\,\alpha^2 x^2\right) \quad \text{with} \quad N = \left(\frac{\alpha^2}{\pi}\right)^{1/4}.$$

To calculate Δx we need

$$\begin{aligned}
\langle x\rangle &= \int_{-\infty}^{\infty} dx\ \psi^*(x)\,x\,\psi(x) = 0 \\
\langle x^2\rangle &= \int_{-\infty}^{\infty} dx\ \psi^*(x)\,x^2\,\psi(x) = N^2 \int_{-\infty}^{\infty} dx\ x^2\,\exp\left(-\alpha^2 x^2\right) \\
&= -\frac{N^2}{2\alpha^2}\int_{-\infty}^{\infty} dx\ x\,d\left(\exp\left(-\alpha^2 x^2\right)\right) = \frac{N^2}{2\alpha^2}\int_{-\infty}^{\infty} dx\ d\left(\exp\left(-\alpha^2 x^2\right)\right) = \frac{1}{2\alpha^2}.
\end{aligned}$$

Thus $\Delta x = \sqrt{\langle(x - \langle x\rangle)^2\rangle} = 1/\alpha\sqrt{2}$. The uncertainty Δp_x is found using the momentum operator $-i\hbar\,d/dx$ or using the momentum space wave function,

$$\tilde{\psi}(p) = \tilde{N}\,\exp\left(-\frac{1}{2}\,\frac{p^2}{\alpha^2\hbar^2}\right) \quad \text{with} \quad \tilde{N} = \left(\frac{1}{\pi\alpha^2\hbar^2}\right)^{1/4},$$

yielding

$$\begin{aligned}
\langle p_x\rangle &= 0, \\
\langle p_x^2\rangle &= \frac{\alpha^2\,\hbar^2}{2},
\end{aligned}$$

leading to $\Delta p_x = \alpha\hbar/\sqrt{2}$. Thus for the harmonic oscillator one finds $\Delta x\,\Delta p_x = \hbar/2$, which is in agreement with the uncertainty relation. Actually a Gaussian wave function is the only one that reaches the equal sign in this uncertainty relation.

The uncertainty of two noncompatible observables of course could still be zero if the expectation value of the commutator vanishes. An example is $\Delta\ell_x\,\Delta\ell_y$ for an $\ell = 0$ state (s-wave).

11.2 The Heisenberg energy-time uncertainty relation

In quantum mechanics one also often refers to the energy-time uncertainty. This, however, is fundamentally different from the uncertainty relations discussed above, since time in quantum mechanics has nothing to do with an operator. We have seen, however, that in cases where the energy of a system is not fixed or known, the expectation value of operators oscillates. If two energies E_1 and E_2 are involved (one could say that there is an energy uncertainty $\delta E \sim E_1 - E_2$), the oscillations involve sine's or cosines with argument $(E_1 - E_2)t/\hbar$. This implies that after a time $\delta t \sim (E_1 - E_2)/\hbar$ (one may argue about the precise proportionality being 1 or $\pi/2$) the system changes its state. Thus

$$\delta E\,\delta t \geq \hbar. \tag{234}$$

This relation thus relates the energy dispersion to the lifetime. It will come back in many applications, e.g. in the emission of photons in case of transitions of electrons between different levels in hydrogen. If the lifetime of the electron in a particular state is τ, the measured energies of the photon show a shape that has a typical *energy width* $\Gamma \sim \hbar/\tau$.

11.3 Creation and annihilation operators

The harmonic oscillator can be solved in a representation independent way. Starting with the hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2, \tag{235}$$

with as starting point the noncommuting operators

$$[x,p] = i\hbar, \tag{236}$$

one introduces

$$a = x\sqrt{\frac{m\omega}{2\,\hbar}} + i\,p\sqrt{\frac{1}{2\,m\omega\,\hbar}} \tag{237}$$

$$a^\dagger = x\sqrt{\frac{m\omega}{2\,\hbar}} - i\,p\sqrt{\frac{1}{2\,m\omega\,\hbar}} \tag{238}$$

satisfying

$$[a,a^\dagger] = 1. \tag{239}$$

The hamiltonian can be expressed in the number operator $N = a^\dagger a$,

$$\begin{aligned} H &= \hbar\omega\left\{\left(x\sqrt{\frac{m\omega}{2\,\hbar}} - i\,p\sqrt{\frac{1}{2\,m\omega\,\hbar}}\right)\left(x\sqrt{\frac{m\omega}{2\,\hbar}} + i\,p\sqrt{\frac{1}{2\,m\omega\,\hbar}}\right) - \frac{i}{2}\frac{[x,p]}{\hbar}\right\} \\ &= \hbar\omega\left\{a^\dagger a + \frac{1}{2}\right\} = \hbar\omega\left\{N + \frac{1}{2}\right\}. \end{aligned} \tag{240}$$

It is straightforward to find the commutation relations between N and a and $a^\dagger$,

$$[N,a^\dagger] = a^\dagger, \quad \text{and} \quad [N,a] = -a. \tag{241}$$

Defining states $|n\rangle$ as eigenstates of N with eigenvalue n, $N|n\rangle = n|n\rangle$ one finds

$$\begin{aligned} N\,a^\dagger|n\rangle &= (n+1)\,a^\dagger|n\rangle, \\ N\,a|n\rangle &= (n-1)\,a|n\rangle \end{aligned}$$

i.e. $a^\dagger$ and a act as raising and lowering operators. From the normalizations one obtains $a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle$ and $a|n\rangle = \sqrt{n}\,|n-1\rangle$, and we see that a state $|0\rangle$ must exist for which $N|0\rangle = a|0\rangle = 0$. In this way one has found for the harmonic oscillator the spectrum of eigenstates $|n\rangle$ (with n a non-negative integer) with $E_n = (n+1/2)\hbar\omega$.

Exercises

Exercise 11.1

Check the uncertainty relation for the groundstate wave function of Hydrogen. The necessary expectation values have been calculated in previous exercises.

Exercise 11.2

Compare the results of the measurements of ℓ_x and ℓ_y for a system described by a wave function with angular dependence of the form

$$\psi \propto \frac{x+i\,y}{\sqrt{2}}.$$

(a) What is the average outcome of the measurements and what are the standard deviations for the measurements.

(b) What does the uncertainty relation tell us about the product of these standard deviations.

(c) Show that the standard deviations found in (a) are consistent with the uncertainty relation in (b).

Exercise 11.3

The creation ($a^\dagger$) and annihilation (a) operators for a one-dimensional harmonic oscillator are defined by

$$a = \frac{1}{\sqrt{2\hbar m\omega}}(m\omega x + ip), \qquad a^\dagger = \frac{1}{\sqrt{2\hbar m\omega}}(m\omega x - ip).\,.$$

The eigenstates $|n\rangle$ of H are assumed to be normalised.

(a) Show that $a^\dagger|n\rangle = c_n|n+1\rangle$ and calculate c_n.

(b) Show that $a|n\rangle = d_n|n-1\rangle$ and calculate d_n.

Assume that the operator $B(a,a^\dagger)$ contains a product of creation and annihilation operators, e.g. $B(a,a^\dagger) = aaa^\dagger aa^\dagger \ldots aa^\dagger$.

(c) Explain that $\langle n|B(a,a^\dagger)|n\rangle >= 0$ unless $B(a,a^\dagger)$ contains as many creation as annihilation operators.

(d) How many creation and annihilation must B have to find a nonzero result for $\langle m|B(a,a^\dagger)|n\rangle$.

(e) Calculate the following matrix elements

$$\langle n|x|m\rangle\ , \quad \langle n|x^2|m\rangle\ , \quad \langle n|p|m\rangle \text{ en } \langle n|p^2|m\rangle.$$

(f) Calculate Δx and Δp for an eigenstate $|n\rangle$ of H and check the uncertainty relation.

12 Inversion symmetry

12.1 The space inversion operation

For coordinates, inversion means:

$$\boldsymbol{r} \longrightarrow -\boldsymbol{r} \qquad \text{and} \qquad t \longrightarrow t, \tag{242}$$

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

$$\boldsymbol{p} \longrightarrow -\boldsymbol{p} \qquad \text{and} \qquad \boldsymbol{\ell} \longrightarrow \boldsymbol{\ell}. \tag{243}$$

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

$$H(\boldsymbol{r}, \boldsymbol{p}, \ldots) = H(-\boldsymbol{r}, -\boldsymbol{p}, \ldots). \tag{244}$$

Since the kinetic part of the hamiltonian usually is quadratic in the momentum, that part is invariant, thus one can look at the potential. Examples of invariant hamiltonians are the case of one particle in a central potential $V(|\boldsymbol{r}|)$, or the situation of one electron in a diatomic molecule with a potential $V(\boldsymbol{r}) = V_1(|\boldsymbol{r}+\boldsymbol{a}|) + V_2(|\boldsymbol{r}-\boldsymbol{a}|)$. The latter potential is invariant under inversion only for the case that $V_1 = V_2$.

Consider now an eigenstate of an invariant hamiltonian,

$$H(\boldsymbol{r}, \boldsymbol{p})\phi(\boldsymbol{r}) = E\phi(\boldsymbol{r}) \tag{245}$$

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

$$H(-\boldsymbol{r}, -\boldsymbol{p})\phi(-\boldsymbol{r}) = E\phi(-\boldsymbol{r}) \tag{246}$$

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

$$H(\boldsymbol{r}, \boldsymbol{p})\phi(-\boldsymbol{r}) = E\phi(-\boldsymbol{r}). \tag{247}$$

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 combination $a\,\phi_1 + b\,\phi_2$ has also energy E, in particular

$$\phi_\pm(\boldsymbol{r}) = \phi(\boldsymbol{r}) \pm \phi(-\boldsymbol{r}) \tag{248}$$

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

12.2 Inversion and the Parity operator

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, $\boldsymbol{r} \rightarrow -\boldsymbol{r}$ and $t \rightarrow t$, in the case of more particles generalized to $\boldsymbol{r}_i \rightarrow -\boldsymbol{r}_i$ and $t \rightarrow t$. What is happening in the Hilbert space of wave functions. We can just define the action on functions, $\psi \rightarrow \psi' \equiv P\psi$ in such a way that $\psi'(\boldsymbol{r}') = \psi(\boldsymbol{r})$. This means for inversion

$$P\phi(-\boldsymbol{r}) \equiv \phi(\boldsymbol{r}) \quad \Longrightarrow \quad P\phi(\boldsymbol{r}) = \phi(-\boldsymbol{r}). \tag{249}$$

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,

$$P\phi_\pi(\boldsymbol{r}) = \pi\,\phi_\pi(\boldsymbol{r}) \tag{250}$$

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

$$A \longrightarrow PAP^{-1}. \tag{251}$$

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

$$\hat{\boldsymbol{r}} \longrightarrow P\hat{\boldsymbol{r}}P^{-1} = -\hat{\boldsymbol{r}}, \tag{252}$$

$$\hat{\boldsymbol{p}} \longrightarrow P\hat{\boldsymbol{p}}P^{-1} = -\hat{\boldsymbol{p}}, \tag{253}$$

$$\hat{\boldsymbol{\ell}} \longrightarrow P\hat{\boldsymbol{\ell}}P^{-1} = +\hat{\boldsymbol{\ell}}, \tag{254}$$

$$\hat{H}(\hat{\boldsymbol{r}},\hat{\boldsymbol{p}}) \longrightarrow P\hat{H}(\hat{\boldsymbol{r}},\hat{\boldsymbol{p}})P^{-1} = \hat{H}(-\hat{\boldsymbol{r}},-\hat{\boldsymbol{p}}). \tag{255}$$

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

$$PHP^{-1} = H \quad \Longleftrightarrow \quad [P,H] = 0. \tag{256}$$

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

12.3 Applications

Bound states in one dimension

For the one-dimensional hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{d}{dx^2} + V(x), \tag{257}$$

with a symmetric potential $V(x) = V(-x)$, one finds by doing the explicit calculation that the solutions separate 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.

Particle in a central potential

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

$$H = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(r). \tag{258}$$

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,

  $$\phi(\boldsymbol{r}) = \frac{u_{n\ell}(r)}{r}\,Y_\ell^m(\theta,\varphi). \tag{259}$$

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

  $$Y_\ell^m(\theta,\varphi) \;\longrightarrow\; Y_\ell^m(\pi-\theta,\varphi+\pi) = (-)^\ell\,Y_\ell^m(\theta,\varphi). \tag{260}$$

  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.

Electrons in atoms

The hamiltonian for Z electrons in atoms is given by

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{Z}\boldsymbol{\nabla}_i^2 + \sum_{i=1}^{Z}\frac{-Ze^2}{4\pi\epsilon_0\,r_i} + \sum_{i>j}^{Z}\frac{e^2}{4\pi\epsilon_0\,|\boldsymbol{r}_i - \boldsymbol{r}_j|}. \tag{261}$$

- 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 in that case is the product of the single-electron wave functions (as in Eq. 259),

$$\phi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_Z)=\prod_{i=1}^{Z}\phi_{n_i\ell_i m_i}(\boldsymbol{r}_i), \tag{262}$$

$$E=\sum_{i=1}^{Z}E_{n_i\ell_i}, \tag{263}$$

- The parity of this eigenfunctions is

$$\pi=\prod_{i=1}^{Z}\pi_i=\prod_{i=1}^{Z}(-)^{\ell_i}=(-)^{\sum_i\ell_i}. \tag{264}$$

  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 operator and selection rules

An operator that is often encountered in connection with light emission or absorption is the electric dipole moment operator,

$$\boldsymbol{D}=-\sum_i e_i\,\boldsymbol{r}_i. \tag{265}$$

Its behavior under parity is

$$\boldsymbol{D}\longrightarrow P\boldsymbol{D}P^{-1}=-\boldsymbol{D}. \tag{266}$$

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* $\boldsymbol{D}$ *it is even simpler*
>
> $$\langle\boldsymbol{D}\rangle=\langle\phi|\boldsymbol{D}|\phi\rangle=\underbrace{\langle\phi|P^{-1}}_{\pi\langle\phi|}\underbrace{P\boldsymbol{D}P^{-1}}_{-\boldsymbol{D}}\underbrace{P|\phi\rangle}_{\pi|\phi\rangle}=-\pi^2\,\langle\phi|\boldsymbol{D}|\phi\rangle=-\langle\boldsymbol{D}\rangle$$

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

$$\langle f|\boldsymbol{D}|i\rangle=\underbrace{\langle f|P^{-1}}_{\pi_f\langle f|}\underbrace{P\boldsymbol{D}\,P^{-1}}_{-\boldsymbol{D}}\underbrace{P|i\rangle}_{\pi_i|i\rangle}=-\pi_i\pi_f\,\langle f|\boldsymbol{D}|i\rangle, \tag{267}$$

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.

A diatomic molecule

The hamiltonian for electrons in a diatomic molecule is given by

$$H = -\frac{\hbar^2}{2m}\sum_i \boldsymbol{\nabla}_i^2 + \sum_i \frac{-Z_1 e^2}{4\pi\epsilon_0\,|r_i + \boldsymbol{a}|} + \sum_i \frac{-Z_2 e^2}{4\pi\epsilon_0\,|r_i - \boldsymbol{a}|} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0\,|\boldsymbol{r}_i - \boldsymbol{r}_j|}. \tag{268}$$

- 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.

Questions

1. Show that invariance of angular momentum $\boldsymbol{\ell}$ under inversion implies that angular momentum and parity are compatible. This implies that angular momentum eigenstates have definite parity.
2. Show that for quadrupole transitions, proceeding via quadrupole operators of the form $Q_{kl} = e\, r_k r_l$ (indices k and l indicate the components) one must have $\pi_i = \pi_f$.

13 Translation symmetry

13.1 The generating operators for translations

Let us start with translation symmetry for one dimension,

$$x \longrightarrow x' = x + a. \tag{269}$$

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 with a wave function. For continuous transformations, it turns out to be extremely useful to study first the infinitesimal problem (in general true for so-called Lie transformations). We then get for small a

$$\phi(x+a) = \phi(x) + a\,\frac{d\phi}{dx} + \ldots = \underbrace{\left(1 + \frac{i}{\hbar}\,a\,p_x + \ldots\right)}_{U(a)}\phi(x) \tag{270}$$

which defines the shift operator $U(a)$ of which the momentum operator $p_x = -i\hbar\,\frac{d}{dx}$ is the *generator.*

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,

$$H(x+a) = H(x) + a\,\frac{dH}{dx} + \ldots = H(x) + \frac{i}{\hbar}\,a\,[p_x, H] + \ldots. \tag{271}$$

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

$$\begin{aligned}
[p_x, H]\phi(x) &= p_x(H\phi)(x) - H(p_x\phi)(x) \\
&= -i\hbar\left\{\frac{d}{dx}\,(H(x)\phi(x)) - H(x)\,\frac{d\phi}{dx}\right\} \\
&= -i\hbar\left(\frac{dH}{dx}\right)\phi(x).
\end{aligned} \tag{272}$$

The important conclusion is that translation invariance implies

$$H(x+a) = H(x) \iff [p_x, H] = 0. \tag{273}$$

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

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

we find that

$$H(x+a) = U(a)\,H(x)\,U^{-1}(a), \tag{274}$$

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

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

> *A useful (general) relation for operators is the following. Consider operators A, B and O. If O is given by*
>
> $$O(c) = e^{cA}\,B\,e^{-cA},$$
>
> *where c is a parameter, then*
>
> $$\frac{dO}{dc} = e^{cA}\,[A,B]\,e^{-cA}.$$

Translation invariance can easily be generalized to three coordinates of one particle and to more particles by considering

$$\boldsymbol{r}_i \longrightarrow \boldsymbol{r}_i' = \boldsymbol{r}_i + \boldsymbol{a}. \tag{275}$$

The shift operator is

$$\begin{aligned} U(\boldsymbol{a}) &= \exp\left(+\boldsymbol{a}\cdot\sum_i \boldsymbol{\nabla}_i\right) = \exp\left(+\frac{i}{\hbar}\,\boldsymbol{a}\cdot\sum_i \boldsymbol{p}_i\right) = \exp\left(-\frac{i}{\hbar}\,\boldsymbol{a}\cdot\boldsymbol{P}\right) \\ &= 1+\boldsymbol{a}\cdot\sum_i\boldsymbol{\nabla}_i+\ldots = 1+\frac{i}{\hbar}\,\boldsymbol{a}\cdot\sum_i\boldsymbol{p}_i+\ldots = 1+\frac{i}{\hbar}\,\boldsymbol{a}\cdot\boldsymbol{P}+\ldots, \end{aligned} \tag{276}$$

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 of the whole world implies that

$$U(\boldsymbol{a})\,H\,U^{-1}(\boldsymbol{a}) = H \iff [\boldsymbol{P},H] = 0. \tag{277}$$

Thus a translation-invariant Hamiltonian usually does not commute with the momenta of individual particles or with relative momenta, but only with the total momentum operator (center of mass momentum), of which the expectation value thus is conserved.

13.2 Applications

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 $E = p^2/2m$.

Two-particle system

The two-particle system with the hamiltonian

$$H = \frac{\boldsymbol{p}_1^2}{2m_1} + \frac{\boldsymbol{p}_2^2}{2m_2} + V(\boldsymbol{r}_1 - \boldsymbol{r}_2) \tag{278}$$

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,

$$H = \frac{\boldsymbol{P}^2}{2M} + \frac{\boldsymbol{p}^2}{2\mu} + V(\boldsymbol{r}) \tag{279}$$

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

$$\Phi(\boldsymbol{R}, \boldsymbol{r}) = \exp\left(\frac{i}{\hbar}\,\boldsymbol{P}\cdot\boldsymbol{R}\right)\,\phi_{\rm rel}(\boldsymbol{r}).$$

Bloch theorem

Consider a periodic potential (in one dimension), $V(x+d) = V(x)$. One has a periodic Hamiltonian that commutes with the (unitary) shift operator $U(d) = \exp(+i\,d\,p_x/\hbar)$,

$$[H, U(d)] = 0 \tag{280}$$

These thus have a common set of eigenstates ϕ_{nk}, satisfying $H\,\phi_{n\,k}(x) = E_n\,\phi_{n\,k}(x)$ and $U(d)\,\phi_{n\,k}(x) = e^{i\,kd}\,\phi_{n\,k}(x)$ in which kd runs (for instance) between $-\pi \le kd \le \pi$. Using that $U(d)$ is the translation operator, one finds that

$$\phi_{n\,k}(x+d) = e^{i\,kd}\,\phi_{n\,k}(x) \tag{281}$$

Equivalently by writing ϕ as the *Bloch wave*

$$\phi_{n\,k}(x) \equiv e^{ikx}\,u_{n\,k}(x) \tag{282}$$

one finds that $u_{n\,k}(x)$ is periodic, satisfying $u_{n\,k}(x+d) = u_{n\,k}(x)$.

13.3 Time evolution

In the same way as for translations one sees that

$$|\psi(t)\rangle = \left(1 + t\frac{d}{dt} + \ldots\right)|\psi(0)\rangle = \exp\left(-\frac{i}{\hbar}\,tH\right)|\psi(0)\rangle, \tag{283}$$

which is nothing else as the time-dependent Schrödinger equation stated in Eq. 23. Thus in the same way as the momentum is the generator of space translations, the Hamiltonian is the generator of time translations. If we know this generator in terms of other quantities (operators in quantum mechanics) one has the starting point of any theory. In classical mechanics you may have seen how to obtain the Hamiltonian (momentum) from the Lagrangian as a conserved quantity related to time (space) translation invariance.

Questions and exercises

Exercise 13.1

Prove Eq. 280 for a periodic potential.

Exercise 13.2

We consider the periodic version of the delta function potential in Exercise 3.5, i.e. $V(x+n\,d) = V(x)$ for integer n (d can be considered as the *lattice spacing* starting with

$$V(x) = -\frac{\hbar^2}{m\,a}\,\delta(x)$$

near zero [See section 7.3 for the properties of the delta-function]. One has the condition

$$\lim_{x\downarrow 0}\phi'(x) - \lim_{x\uparrow 0}\phi'(x) = -\frac{2\,\phi(0)}{a},$$

and the same condition around any point $n\,d$ ($n \in \mathbb{Z}$). We have found in this section that the solutions satisfy $\phi_{n\,k}(x+d) = e^{i\,kd}\,\phi_{n\,k}(x)$ (Bloch condition).

(a) Without loss of generality we can choose $\phi_{..k}(0) = 1$ and $\phi_{..k}(d) = e^{i\,kd}$. Determine the most general solution in $0 \le x \le d$ writing

$$\phi_{E,k}(x) = A\,e^{i\,qx} + B\,e^{-i\,qx} \quad \text{with} \quad E = \frac{\hbar^2\,q^2}{2m}$$

or

$$\phi_{E,k}(x) = A\,e^{\kappa x} + B\,e^{-\kappa x} \quad \text{with} \quad E = -\frac{\hbar^2\,\kappa^2}{2m}$$

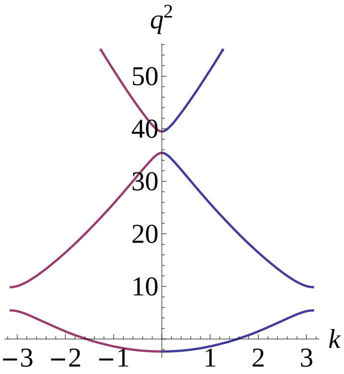
(note: $\kappa = i\,q$).

(b) Calculate the derivatives $\phi'(\epsilon)$ and $\phi'(-\epsilon$ (note the domain for which the expressions in (a) can be used!) and take the limit $\epsilon \to 0$.

(c) Use this to derive the condition on q (or κ) and k,

$$qa = \frac{\sin(qd)}{\cos(qd) - \cos(kd)} \qquad \text{or} \qquad \kappa a = \frac{\sinh(\kappa d)}{\cosh(\kappa d) - \cos(kd)}.$$

(d) Shown at the right is the dispersion $E(k)$ found under (c) or actually q^2d^2 plotted as function of kd for the case $a = d$. The model is suitable to study the *band structure* in solids (Do you understand why?). Study the band structure for some other values of a (look at $a < d$ and $a > d$ (What corresponds to tight binding or weak binding?). What do you notice (look at band gaps, compare with free dispersion relation and bound state energy).



(e) Assume that the one-dimensional system would consist of a finite number (N) of potential dips, e.g. a circular configuration. How many k-values are allowed in that case?

14 Rotation symmetry

14.1 The generating operators for rotations

Rotations are characterized by a rotation axis and an angle,

$$\boldsymbol{r} \longrightarrow R(\hat{n},\alpha)\,\boldsymbol{r}, \tag{284}$$

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

$$\left(\begin{array}{c} x \\ y \\ z \end{array}\right) \longrightarrow \left(\begin{array}{ccc} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{array}\right)\left(\begin{array}{c} x \\ y \\ z \end{array}\right). \tag{285}$$

This also gives rise to transformations in the Hilbert space of wave functions. For a rotation around the z-axis it is convenient to use polar coordinates. We then find

$$\begin{aligned} \phi(r,\theta,\varphi+\alpha) &= \phi(r,\theta,\varphi) + \alpha\,\frac{\partial}{\partial\varphi}\,\phi + \ldots \\ &= \left(1 + \frac{i}{\hbar}\,\alpha\left(-i\hbar\,\frac{\partial}{\partial\varphi}\right) + \ldots\right)\phi \\ &= \left(1 + \frac{i}{\hbar}\,\alpha\,\ell_z + \ldots\right)\phi, \end{aligned} \tag{286}$$

from which one concludes that ℓ_z is the generator of rotations around the z-axis, and the rotation operator in the Hilbert space is

$$U(\hat{z},\alpha) = \exp\left(+\frac{i}{\hbar}\,\alpha\,\ell_z\right) = 1 + \frac{i}{\hbar}\,\alpha\,\ell_z + \ldots\ . \tag{287}$$

As for the translations, an operator behaves as

$$\begin{aligned} H(r,\theta,\varphi+\alpha) &= H(r,\theta,\varphi) + \alpha\,\frac{\partial H}{\partial\varphi} + \ldots \\ &= H + \frac{i}{\hbar}\,\alpha\,[\ell_z, H] + \ldots \\ &= U(\hat{z},\alpha)\,H\,U^{-1}(\hat{z},\alpha). \end{aligned} \tag{288}$$

Rotational invariance (around z-axis) implies that

$$U(\hat{z},\alpha)\,H\,U^{-1}(\hat{z},\alpha) = H \iff [\boldsymbol{\ell}_z, H] = 0. \tag{289}$$

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

$$e^A\, e^B = e^C \quad \textit{with} \quad C = A + B + \frac{1}{2}\,[A,B] + \frac{1}{12}[A,[A,B]] + \frac{1}{12}[B,[A,B]] + \ldots\ .$$

(Baker-Campbell-Hausdorff relation)

For more particles, invariance under rotations of the world implies

$$H \text{ invariant} \Longleftrightarrow [\boldsymbol{L}, H] = 0, \tag{290}$$

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

14.2 Applications

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.

Two-particle system

For the two-particle hamiltonian of Eq. 278 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

$$\Phi(\boldsymbol{R}, \boldsymbol{r}) = \exp\left(\frac{i}{\hbar}\,\boldsymbol{P}\cdot\boldsymbol{R}\right)\,\frac{u_{n\ell m}(r)}{r}\, Y_\ell^m(\theta, \varphi).$$

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

  $$P_{xz}\phi(x,y,z) = \phi(x,-y,z) \tag{291}$$

  (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* (-).

Exercises

Exercise 14.1

Given the (three dimensional) Hamiltonian

$$H = \frac{\boldsymbol{p}^2}{2m} + \frac{1}{2}\,m\omega^2(x^2+y^2).$$

(a) Determine from the symmetries of this Hamiltonian as many compatible operators as possible and give mutually compatible sets of operators.

(b) Indicate the expected spatial behavior of the wave function. Do this by using different possibilities for the choice of coordinates (Cartesian, cylindric, polar, ... coordinates) and using the results of (a).

(c) Discuss the discrete states in the spectrum of this Hamiltonian including the degeneracy of the lowest few states.

15 Identical particles

15.1 Permutation symmetry

The hamiltonian for Z electrons in an atom,

$$H(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_Z; \boldsymbol{p}_1, \ldots, \boldsymbol{p}_Z) = \sum_{i=1}^{Z} \left(-\frac{\hbar^2}{2m} \boldsymbol{\nabla}_i^2 - \frac{Ze^2}{4\pi\epsilon_0 \, r_i} \right) + \sum_{i>j}^{Z} \frac{e^2}{4\pi\epsilon_0 \, |\boldsymbol{r}_i - \boldsymbol{r}_j|} \tag{292}$$

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

$$H(1 \ldots i \ldots j \ldots Z) = H(1 \ldots j \ldots i \ldots Z). \tag{293}$$

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 $\phi(1,2)$ and $\phi(2,1)$. In particular we can choose symmetric and antisymmetric combinations

$$\phi^{S/A} = \phi(12) \pm \phi(21), \tag{294}$$

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,

$$\phi^S = \phi(123) + \phi(213) + \phi(231) + \phi(321) + \phi(312) + \phi(132), \tag{295}$$

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

$$\phi^S = \phi(123) - \phi(213) + \phi(231) - \phi(321) + \phi(312) - \phi(132), \tag{296}$$

(any permutation operator gives back minus the wave function) and there are four combinations with mixed symmetry. Nature is kind and only allows the symmetric or antisymmetric function according to the socalled

spin-statistics theorem: for a system of identical particles one has either *symmetric* wave functions (*Bose-Einstein statistics*) or *antisymmetric* wave function (*Fermi-Dirac statistics*). For identical particles obeying Bose-Einstein statistics the wave function does not change under interchange of any two particles. Such particles are called *bosons*. For particles obeying Fermi-Dirac statistics the wave function changes sign under a permutation of any two particles. Such particles are called *fermions*. In the next section we will discuss spin. Particles with integer spin are bosons, particles with half-integer spin are fermions.

For instance electrons which have spin 1/2 (two possible spin states) are fermions. 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,

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

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 reside in the same state, while any two fermions cannot be in the same state, known as the *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*
>
> $$\phi^A(123) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_a(1) & \phi_a(2) & \phi_a(3) \\ \phi_b(1) & \phi_b(2) & \phi_b(3) \\ \phi_c(1) & \phi_c(2) & \phi_c(3) \end{vmatrix}.$$

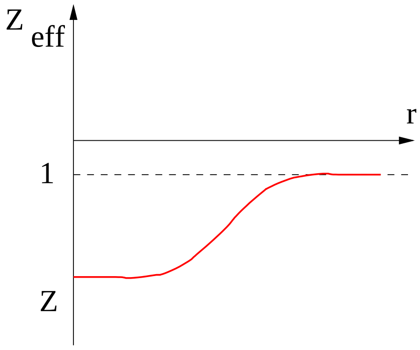
15.2 Applications

Bose-Einstein condensates

Bosons can reside in the same state. For instance by cooling down a gas of bosons they can all have momentum $\boldsymbol{p} = 0$. The wave function in momentum space would be a delta function, $\delta(\boldsymbol{p})$, leading to a single multi-boson system with macroscopic extension (in theory infinite for a true delta-function) in which all particles have lost their identity.

Atomic structure

The most well-known application of Fermi-Dirac statistics is the consecutive filling of atomic levels giving the periodic table of elements. For many-electron atoms a good starting point is trying to approximate the average effect of the electron-electron repulsion term in Eq. 292 into an effective central potential. The effective charge felt by an electron is expected to behave like

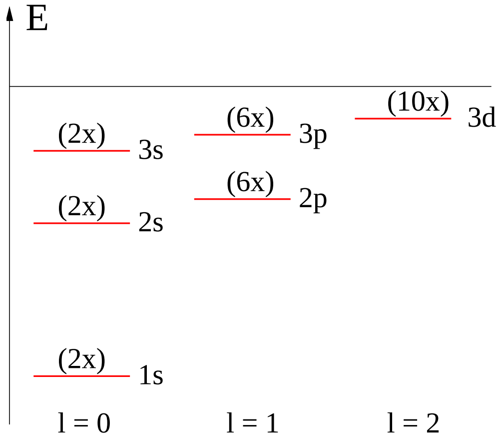


$$Z_{\text{eff}} \left\{ \begin{array}{l} \xrightarrow{r\to\infty} 1 \\ \xrightarrow{r\to 0} Z \end{array} \right.$$

The behavior of $Z_{\text{eff}}(r)$ can e.g. be obtained from the electron densities in a self-consistent matter. Thus, one can approximate the many-electron hamiltonian by

$$H(\boldsymbol{r}_1,\dots,\boldsymbol{r}_Z;\boldsymbol{p}_1,\dots,\boldsymbol{p}_Z) \approx \sum_{i=1}^{Z}\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}_i^2 - \frac{Z_{\text{eff}}(r)\,e^2}{4\pi\epsilon_0\,r_i}\right) + \dots \tag{297}$$

The advantage of this procedure is that part of the repulsion is taken into account retaining a central interaction and a separable hamiltonian. This will modify the spectrum, lifting the degeneracy between different ℓ-values for given n. In general the higher ℓ values will because of the angular momentum contribution $\hbar^2\,\ell(\ell+1)/2m\,r^2$ in the effective radial potential will feel a smaller charge and hence become less bound.



The (schematic) spectrum for many-electron atoms. A possible parametrization of the levels taking into account the screening effect is

$$E_{n\ell} = -\frac{R_\infty}{(n-\delta_\ell)^2},$$

where δ_ℓ is referred to as quantum defect, and one expects $\delta_\ell \to 0$ for large ℓ-values. This will work particularly well for atoms with one electron outside a closed shell.

In the central field approximation, the hamiltonian is separable for the different electrons and the solution is an antisymmetrized product of single electron states (Slater determinant), where one needs to keep in mind the spin degeneracy (2 for each level). Operators compatible with the hamiltonian are $\boldsymbol{\ell}_i$ (and similarly spin operators), just as is the parity operator. Hence one has many good quantum numbers. At this level of approximation one can label the states by giving the various $(n\ell)$ levels and their multiplicities, e.g. for the ground state of helium $(1s)^2$, for Carbon $(1s)^2(2s)^2(2p)^2$, etc. Combining the angular momenta and spins into specific multiplets will be discussed as an application of spin but is not yet relevant, since all states are at this stage degenerate. This remains true if one refines the picture by using an effective central charge $Z_{\text{eff}}(r)$. The only effect of the latter is the splitting of different ℓ-values corresponding to the same principal quantum number n.

The structure of the periodic table is summarized in the table given below with the levels given in order of increasing energy. In this table the noble gases correspond to situations in which there are large energy gaps between the filled shell and the next available one. Characteristics of these noble gases are a high ionization energy and a small affinity to other elements, e.g. $E_{\text{ionization}} = 24.6$ eV (He), 21.6 eV (Ne) and 15.8 eV (Ar). The level scheme in the table can also be used to establish the excited states.

n							summed # of levels	remarks
1	2	3	4	5	6	7		
$(1s)^2$							2 (He)	
	$(2s)^2$						4	
	$(2p)^6$						10 (Ne)	
		$(3s)^2$					12	
		$(3p)^6$					18 (Ar)	
			$(4s)^2$				20	
		$(3d)^{10}$					30	Fe-group
			$(4p)^2$				36 (Kr)	
				$(5s)^2$			38	
			$(4d)^{10}$				48	Pd-group
				$(5p)^6$			54 (Xe)	
					$(6s)^2$		56	
			$(4f)^{14}$				70	Lanthanides
				$(5d)^{10}$			80	Pt-group
					$(6p)^6$		86 (Rn)	
						$(7s)^2$	88	
				$(5f)^{14}$			102	Actinides
					$(6d)^{10}$		112	Pt-group
						$(7p)^6$	118 (?)	

Exercises

Exercise 15.1

Given the infinite square well potential (one dimension)

$$V(x) = \begin{cases} \infty & |x| > a \\ 0 & |x| \leq a \end{cases} .$$

(a) Calculate the energy of the ground state for N non-selfinteracting bosons.

(b) Calculate the energy of the groundstate for N non-selfinteracting fermions.

Exercise 15.2

Two (one-dimensional) particles can be in orthonormal states a or b with wave functions ϕ_a and ϕ_b.

(a) Determine the two-body wave function $\phi(x_1, x_2)$ if (i) the particles are distinguishable and particle 1 is in state a, while particle 2 is in state b; (ii) the particles are indistinguishable bosons; (iii) the particles are indistinguishable fermions.

(b) Express, for all three cases under (a) the expectation value $\langle\phi|(x_1 - x_2)^2|\phi\rangle$ in matrix elements for the states ϕ_a and ϕ_b. Work out the problem, so you can compare the three cases.

(c) Explain from the answer in (b) that identical bosons tend to attract each other, while identical fermions tend to repel each other.

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

$$[s_i, s_j] = i\hbar\epsilon_{ijk}\, s_k, \tag{298}$$

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

$$\left.\begin{array}{l}[\ell_i, S] = 0\\ [\ell_i, V_j] = i\hbar\,\epsilon_{ijk}\, V_k\end{array}\right\} \text{ for a single particle without spin,} \tag{299}$$

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

$$\boldsymbol{j} \equiv \boldsymbol{\ell} + \boldsymbol{s}, \tag{300}$$

satisfies

$$\left.\begin{array}{l}[j_i, S] = 0\\ [j_i, V_j] = i\hbar\,\epsilon_{ijk}\, V_k,\end{array}\right\} \text{ for a single particle} \tag{301}$$

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

$$\boldsymbol{L} = \sum_{n=1}^{N} \boldsymbol{\ell}_n, \qquad \boldsymbol{S} = \sum_{n=1}^{N} \boldsymbol{s}_n, \qquad \boldsymbol{J} = \sum_{n=1}^{N} \boldsymbol{j}_n = \boldsymbol{L} + \boldsymbol{S}, \tag{302}$$

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

$$\left.\begin{array}{l}[J_i, S] = 0\\ [J_i, V_j] = i\hbar\,\epsilon_{ijk}\, V_k\end{array}\right\} \text{ for an isolated system} \tag{303}$$

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. 303 indeed is a scalar quantity, satifying the required scalar commutation relation.*

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

Rotation invariance of a system of particles requires

$$[\boldsymbol{J}, H] = 0. \tag{304}$$

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 Mandl 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 $\boldsymbol{s}^2 = s_x^2 + s_y^2 + s_z^2$,

$$[s_i, s_j] = i\hbar\,\epsilon_{ijk}\,s_k, \tag{305}$$

$$[\boldsymbol{s}^2, s_i] = 0. \tag{306}$$

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

$$\boldsymbol{s}^2|s,m\rangle = \hbar^2\,s(s+1)|s,m\rangle, \tag{307}$$

$$\boldsymbol{s}_z|s,m\rangle = m\hbar\,|s,m\rangle. \tag{308}$$

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

$$s_\pm \equiv s_x \pm i\,s_y. \tag{309}$$

The commutation relations for these operators are,

$$[\boldsymbol{s}^2, s_\pm] = 0, \tag{310}$$

$$[s_z, s_\pm] = \pm\hbar\,s_\pm, \tag{311}$$

$$[s_+, s_-] = 2\hbar\,s_z, \tag{312}$$

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

$$\begin{aligned} s_+|s,m\rangle &= \hbar\sqrt{s(s+1)-m(m+1)}\,|s,m+1\rangle \\ &= = \hbar\sqrt{(s-m)(s+m+1)}\,|s,m+1\rangle \qquad (313) \\ s_-|s,m\rangle &= \hbar\sqrt{s(s+1)-m(m-1)}\,|s,m-1\rangle \\ &= \hbar\sqrt{(s+m)(s-m+1)}\,|s,m-1\rangle. \qquad (314) \end{aligned}$$

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 313 and 314 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.

16.5 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

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

Using the definition of the quantum numbers in Eq. 308 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 then 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 $|1,+1\rangle$, $|1,0\rangle$ *and* $|1,-1\rangle$ *or*

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

The spin matrices are then easily found,

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

from which also s_x *and* s_y *can be constructed.*

16.6 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 choose an appropriate notation like $|\hat{\boldsymbol{n}}, \pm\rangle$ or two component spinors $\chi^{(s)}_{m_s}(\hat{\boldsymbol{n}})$, shorthand

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

Suppose that we want to write them down in terms of the eigenstates of s_z, given above, $\chi_{+/-}(\hat{\boldsymbol{z}}) = \chi_{\uparrow/\downarrow}$. 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

$$\boldsymbol{s} \cdot \hat{\boldsymbol{n}} = \frac{1}{2}\hbar\boldsymbol{\sigma} \cdot \hat{\boldsymbol{n}} = \frac{\hbar}{2} \left(\begin{array}{cc} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{array}\right). \tag{315}$$

We find the following two eigenstates and eigenvalues

$$\chi_+(\hat{\boldsymbol{n}}) = \left(\begin{array}{c} \cos(\theta/2) \\ \sin(\theta/2) \end{array}\right) \quad \text{with eigenvalue} \quad +\hbar/2,$$
$$\chi_-(\hat{\boldsymbol{n}}) = \left(\begin{array}{c} -\sin(\theta/2) \\ \cos(\theta/2) \end{array}\right) \quad \text{with eigenvalue} \quad -\hbar/2.$$

The probability that given a state χ_+ 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

$$\left|\chi_+^\dagger(\hat{\boldsymbol{n}})\chi_\uparrow\right|^2 = \cos^2(\theta/2).$$

Exercises

Exercise 16.1

(a) Show that from the commutation relations for the orbital angular momentum operators $\boldsymbol{\ell}$ and the with these operators compatible spin operators $\boldsymbol{s}$ (thus $[\ell_i, s_j] = 0$) the commutation relations of the total angular momentum operators $\boldsymbol{j} = \boldsymbol{\ell} + \boldsymbol{s}$ can be obtained.

(b) Show that from $[J_i, A_j] = i\hbar\,\epsilon_{ijk}\,A_k$ and $[J_i, B_j] = i\hbar\,\epsilon_{ijk}\,B_k$ one finds

$$[J_i, \boldsymbol{A}\cdot\boldsymbol{B}] = 0.$$

(You can consider to do this only for J_x).

(c) Calculate

$$[\boldsymbol{J}^2, A_i].$$

(You can also consider doing this only for one component, e.g. A_z)

Exercise 16.2

With the choice of basis states $|s, m_s\rangle$,

$$|1,1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad |1,0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad |1,-1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix},$$

the matrix representations of the spin operators $\boldsymbol{S}$ for a particle with spin 1 become

$$S_x = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}; \quad S_y = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}; \quad S_z = \hbar\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

(a) Show this for S_x and S_z using the known results for the various spin operators working on $|s, m_s\rangle$ states.

(b) Use the commutator $[S_z, S_x]$ to find S_y.

(c) A measurement of S_x gives $+\hbar$. Give the state vector for the particle immediately after the measurement.

17 Combination of angular momenta

Pre-knowledge

If one works with the direct product of two (or more spaces) one has states $|\ \rangle_a$ and $|\ \rangle_b$ for spaces a and b, which could be the spins of two particles, but also the coordinate space and the spin space of one particle, etc. It could be infinite or finite dimensional spaces. The direct product space is the space built from states denoted (interchangeable)

$$|xy\rangle_{ab} = |x\rangle_a \otimes |y\rangle_b = |x\rangle_a |y\rangle_b,$$

If one has a basis $|1\rangle_a$, $|2\rangle_a$, … of space a and a basis $|1\rangle_b$, $|2\rangle_b$, … of space b, it is customary to order the basis in the direct product space as $|11\rangle_{ab}$, $|12\rangle_{ab}$, …, $|21\rangle_{ab}$ $|22\rangle_{ab}$, …, … . From the operators in space a and those in space b, one can construct operators (denoted interchangeable as $\hat{A}_a \otimes \hat{B}_b$ or $\hat{A}_a\,\hat{B}_b$) in the direct product space,

$$(\hat{A}_a \otimes \hat{B}_b)|xy\rangle_{ab} \equiv \hat{A}_a|x\rangle_a \otimes \hat{B}_b|y\rangle.$$

The labels a and b are mostly omitted. If one has matrices

$$\hat{A} = \begin{pmatrix} A_{11} & A_{12} & \ldots \\ A_{21} & A_{22} & \ldots \\ \vdots & \vdots & \ddots \end{pmatrix} \qquad \hat{B} = \begin{pmatrix} B_{11} & B_{12} & \ldots \\ B_{21} & B_{22} & \ldots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

one gets in terms of the ordered basis (given above)

$$\hat{A} \otimes \hat{B} = \left(\begin{array}{ccc|ccc|c} A_{11}B_{11} & A_{11}B_{12} & \ldots & A_{12}B_{11} & A_{12}B_{12} & \ldots & \ldots \\ A_{11}B_{21} & A_{11}B_{22} & \ldots & A_{12}B_{21} & A_{12}B_{22} & \ldots & \ldots \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \ldots \\ \hline A_{21}B_{11} & A_{21}B_{12} & \ldots & A_{22}B_{11} & A_{22}B_{12} & \ldots & \ldots \\ A_{21}B_{21} & A_{21}B_{22} & \ldots & A_{22}B_{21} & A_{22}B_{22} & \ldots & \ldots \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \ldots \\ \hline \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{array}\right).$$

It is easy to see that one can work with the operators in direct spaces independently, e.g. $(\hat{A}\otimes\hat{B})(\hat{C}\otimes\hat{D}) = \hat{A}\hat{C} \otimes \hat{B}\hat{D}$. Operators $\hat{A} \otimes \hat{I}$ and $\hat{I} \otimes \hat{B}$ are commonly denoted just by $\hat{A}$ and $\hat{B}$, because it is usually clear from the context in which space they work.

17.1 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 $\boldsymbol{j} = \boldsymbol{\ell} + \boldsymbol{s}$). Here one combines the $\mathbb{R}^3$ and the spin-space.
- Two electrons with spin (spin operators $\boldsymbol{s}_1$ and $\boldsymbol{s}_2$, combined into $\boldsymbol{S} = \boldsymbol{s}_1 + \boldsymbol{s}_2$). Here we have the product of spin-space for particle 1 and particle 2.
- Two electrons in atomic orbits (orbital angular momenta $\boldsymbol{\ell}_1$ and $\boldsymbol{\ell}_2$ combined into total orbital angular momentum $\boldsymbol{L} = \boldsymbol{\ell}_1 + \boldsymbol{\ell}_2$). Here we have the direct product spaces $\mathbb{R}^3 \otimes \mathbb{R}^3$ for particles 1 and 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

$$\boldsymbol{J} = \boldsymbol{j}_1 + \boldsymbol{j}_2. \tag{316}$$

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

$$|j_1, m_1\rangle \otimes |j_2, m_2\rangle, \tag{317}$$

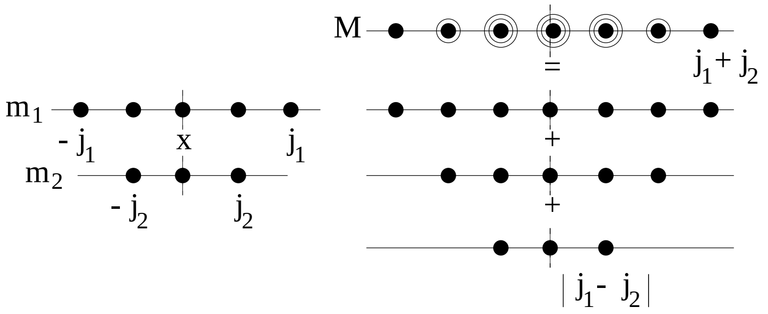
which we can write down since not only $[\boldsymbol{j}_1^2, j_{1z}] = [\boldsymbol{j}_2^2, j_{2z}] = 0$, but also $[j_{1m}, j_{2n}] = 0$. The sum-operator $\boldsymbol{J}$ obviously is not independent, but since the $\boldsymbol{J}$-operators again satisfy the well-known angular momentum commutation 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. 317, $[\boldsymbol{J}^2, j_{1z}] \neq 0$ 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

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

and thus we can relabel the $(2j_1+1)(2j_2+1)$ states in Eq. 317 into states characterized with the quantum numbers

$$|j_1, j_2; J, M\rangle. \tag{318}$$

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

$$J = j_1 + j_2,\ j_1 + j_2 - 1, \ldots, |j_1 - j_2|, \tag{319}$$

going down in steps of one.

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

$$\sum_{J=|j_1-j_2|}^{j_1+j_2} (2J+1) = (2j_1+1)(2j_2+1). \tag{320}$$

Furthermore we have in combining angular momenta:

half-integer with half-integer ⟶ integer
integer with half-integer ⟶ half-integer
integer with integer ⟶ integer

17.2 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. 317,

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

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

$$|1/2, 1/2; 1, +1\rangle = |\uparrow\uparrow\rangle. \tag{321}$$

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

$$|1/2, 1/2; 1, 0\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\Big). \tag{322}$$

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

$$|1/2, 1/2; 1, -1\rangle = |\downarrow\downarrow\rangle. \tag{323}$$

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. 322. 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

$$|1/2, 1/2; 0, 0\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\Big). \tag{324}$$

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 × 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

$$|j_1, j_2; J, M\rangle = \sum_{m_1, m_2} C(j_1, m_1, j_2, m_2; J, M)\, |j_1, m_1\rangle \otimes |j_2, m_2\rangle. \tag{325}$$

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

$$|j_1, m_2\rangle \otimes |j_2, m_2\rangle = \sum_{J,M} C(j_1, m_1, j_2, m_2; J, M)\, |j_1, j_2; J, M\rangle. \tag{326}$$

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 × 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. 322.

We will give two other examples. The first is

1 × 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.

17.3 Applications

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

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

Summarizing in tabular form

Configurations in Helium							
configuration	$E^{(0)}/R_\infty$	L	S	Parity	Symmetry	J-configurations	# states
$(1s)^2$	-8	0	0	+	A	${}^1S_{0^+}$	1
			1	+	S	not allowed	3
$(1s)(2p)$ & $(2p)(1s)$	-5	1	0	−	S/A	${}^1P_{1^-}$	3
			1	−	S/A	${}^3P_{0^-,1^-,2^-}$	9
$(1s)(2s)$ & $(2s)(1s)$	-5	0	0	+	S/A	${}^1S_{0^+}$	1
			1	+	S/A	${}^3S_{1^+}$	3

Important to note is that although additional terms may be present in the full hamiltonian, the solutions found in this way do form a complete set of states for the atom. Other interaction terms give rise to shifts in the zeroth order energies and they may mix the states. To calculate such shifts we need to use perturbation theory.

Atomic multiplets

In a more realistic atom the ee-interaction term (or what remains after taken into account an effective charge) must also be considered. It breaks rotational invariance in the hamiltonian for the electron coordinate $\boldsymbol{r}_i$, thus $\boldsymbol{\ell}_i$ is no longer compatible with the hamiltonian. We note that $\boldsymbol{L}$ is still compatible with the hamiltonian. Since there is no spin-dependence, spin operators $\boldsymbol{s}_i$ and also $\boldsymbol{S}$ are compatible with the hamiltonian and corresponding quantum numbers still can be used.

To illustrate how one easily finds the allowed L and S values given an electron configuration, we consider the ground state configuration of Carbon, $(1s)^2(2s)^2(2p)^2$. The allowed states in a shell can be represented as a number of boxes, e.g. an s-shell as two boxes, a p-shell as six boxes,

$m_s \downarrow\ m_\ell$	0
$+1/2$	
$-1/2$	

$m_s \downarrow\ m_\ell$	-1	0	$+1$
$+1/2$			
$-1/2$			

etc. Putting N electrons in these boxes with at most one electron per box (Pauli principle) one has $6!/N!(6-N)!$ possibilities, e.g. for a filled only one possibility. Obviously then all magnetic quantum numbers combine to zero, $M_L = M_S = 0$ and one also has for the total L and S quantum numbers $L = S = 0$. Hence filled shells can be disregarded for finding total (L, S) values.

As a consequence the specta of atoms with *one* electron outside a closed shell (Li, Na, K, Rb, Cs, Fr) resemble the spectrum of hydrogen, e.g. the configurations for sodium (Na) are $(n\ell)$ with $n \geq 3$. The groundstate for Na is $(3s)^2S_{1/2}$, the first excited states are the $(3p)^2P_{1/2}$ and $(3p)^2P_{3/2}$ levels. The electric dipole transition $^2P \rightarrow ^2S$ is the well-known yellow Na-line in the visible spectrum, which by the fine-structure (see below) is split into two lines corresponding to the transitions $^2P_{3/2} \rightarrow ^2S_{1/2}$ and $^2P_{1/2} \rightarrow ^2S_{1/2}$. For atoms with *two* electrons outside a closed shell (Be, Mg, Ca, Sr, Ba, Ra) the multiplet structure resembles that of helium.

For a particular number of electrons it is easy to look at the number of possibilities to construct particular M_L and M_S values. This is denoted in a Slater diagram

$M_S \downarrow\ M_L$	-2	-1	0	$+1$	$+2$
$+1$	0	1	1	1	0
0	1	2	3	2	1
-1	0	1	1	1	0

It is easy to disentangle this into

$$\underset{(L,S)=(2,0)}{\begin{array}{|c|c|c|c|c|}\hline 0&0&0&0&0\\\hline 1&1&1&1&1\\\hline 0&0&0&0&0\\\hline\end{array}} + \underset{(L,S)=(1,1)}{\begin{array}{|c|c|c|c|c|}\hline 0&1&1&1&0\\\hline 0&1&1&1&0\\\hline 0&1&1&1&0\\\hline\end{array}} + \underset{(L,S)=(0,0)}{\begin{array}{|c|c|c|c|c|}\hline 0&0&0&0&0\\\hline 0&0&1&0&0\\\hline 0&0&0&0&0\\\hline\end{array}}$$

Thus for the Carbon one finds in the groundstate configurations the multiplets

$$^1D \qquad ^3P \qquad ^1S$$

Also for configurations involving more shells that are not completely filled, it is straightforward to find the states in an $M_S - M_L$ diagram. At this point we have completed the quantum number analysis of the spectrum. In order to find the energies one needs to use perturbation theory as well as variational methods to be discussed next. The results of these methods have shown that for the ordering in the spectrum a number of phenomenological rules can be formulated, the *Hund rules.* In particular for the groundstate configuration one has that the terms with highest S-values (highest multiplicity) and then highest L-values have the lowest energy, i.e. in the example for Carbon

$$E(^3P) < E(^1D) < E(^1S).$$

Selection rules

For emission and absorption of light (photons) the relevant operator is the electric dipole operator, which in essence is the position operator. The calculation of transition probabilities are given by the matrix elements between the appropriate states. Since the dipole operator does not involve spin operators, the spin wave function doesn't change in a dipole transition, giving rise to a spin selection rule: $m_{s\,1} = m_{s\,2}$, i.e.

$$\Delta s = \Delta m_s = 0. \tag{327}$$

In fact the photon polarization determines which of the components of the position operator is the relevant operator. Using instead of the Cartesian components, the (spherical) representation of the position vector in terms of the three spherical harmonics with $\ell = 1$, the $Y_1^{m_\gamma}$, one needs (considering one specific electron) the integral

$$\langle 1|\boldsymbol{r}\cdot\boldsymbol{\epsilon}|2\rangle = \sqrt{\frac{4\pi}{3}}\int d^3r\ \psi^*_{n_1\ell_1m_1}(\boldsymbol{r})\,r\,Y_1^{m_\gamma}(\theta,\varphi)\,\psi_{n_2\ell_2m_2}(\boldsymbol{r}),$$

which factorizes into

$$\langle 1|\boldsymbol{r}\cdot\boldsymbol{\epsilon}|2\rangle = \sqrt{\frac{4\pi}{3}}\int dr\ r\,u_{n_1\ell_1}(r)\,u_{n_2\ell_2}(r)\int d\Omega\ Y_{\ell_1}^{m_1\,*}(\theta,\varphi)\,Y_1^{m_\gamma}(\theta,\varphi)\,Y_{\ell_2}^{m_2}(\theta,\varphi).$$

From the φ-dependence of the spherical harmonics one sees that the matrix element is proportional to

$$\int d\varphi\ e^{-i\,m_1\varphi}\,e^{i\,m_\gamma\varphi}\,e^{i\,m_2\varphi} = 2\pi\,\delta(m_2+m_\gamma-m_1),$$

giving rise to the selection rule

$$\Delta m_\ell = 0,\ \pm 1, \tag{328}$$

each of these corresponding to a specific photon polarization. The integral for the φ-dependent part is simple, but more general one can use the properties of the Y_ℓ^m-functions to see what happens with the full angular integration. One only gets a nonzero result if the addition of angular momenta $|\ell_2,m_2\rangle$ and $|1,m_\gamma\rangle$ can yield the final state $|\ell_1,m_1\rangle$ via the well-known angular momentum addition rules. The result is simply proportional to the Clebsch-Gordan coefficient in this recoupling,

$$\langle 1|\boldsymbol{r}\cdot\boldsymbol{\epsilon}|2\rangle = \sqrt{\frac{4\pi}{3}}\int dr\ r\,u_{n_1\ell_1}(r)\,u_{n_2\ell_2}(r)\,C(1,m_\gamma,\ell_2,m_2;\ell_1,m_1).$$

which is known as the Wigner-Eckart theorem. This leads besides the m-selection rule to $|\Delta\ell| \le 1$ Knowing the parity of the spherical harmonics one immediately gets a *parity selection rule*, namely $\Pi_1\Pi_2 = -1$ or with $\Pi = (-)^\ell$, one is left with

$$\Delta\ell = \pm 1. \tag{329}$$

Rotational invariance further requires that the sum of the total angular momentum in initial and final state is conserved. This becomes relevant if the orbital angular momentum and spin of electrons and/or atomic nuclei are coupled to a specific total angular momentum. In many cases the orbital angular momentum then is no longer a good quantum number. Still, even when ℓ and s are coupled to j, or for many particles L and S are coupled to J, the transition operator involves a simple $Y_1^{m_\gamma}$, implying

$$\Delta J = 0,\ \pm 1 \tag{330}$$

(with $J=0 \rightarrow J=0$ forbidden!).

The interactions (absorption or emission) of photons in atoms can also proceed via different operators. The one treated here is known as electric dipole radiation (E1). In order of strength one has also the magnetic dipole radiation (M1), electric quadrupole radiation (E2), etc. For instance electric quadrupole radiation is governed by operators of the type $x_i\,x_j$, i.e. in a spherical representation the $\ell = 2$ spherical harmonics. This leads to transition selection rules in which parity is not changed and since the operators are proportional to $r^2\,Y_2^{m_\gamma}$ one has $\Delta\ell = 2$.

Exercises

Exercise 17.1

Quarks are particles with spin 1/2. Baryons, such as the proton and neutron, are built from three quarks. Mesons, like the pions and kaons, are built from a quark and an antiquark (antiquarks also have spin 1/2). Assume the quarks are in the ground state.

(a) What is the orbital angular momentum of the ground state.

(b) What spin can baryons have?

(c) What spin can mesons have?

(d) What will be the results of (b) and (c) for the total angular momentum of baryons and mesons when we also allow for orbital angular momentum.

(e) What can you tell about the symmetry under the exchange of particles for the wave function of a system composed of baryons (for example an atomic nucleus built from protons and neutrons).

Exercise 17.2

Consider two states with $j_1 = 1$ and $j_2 = 3/2$. The angular momenta of these states can be combined into the total angular momentum J, where for the operators $\boldsymbol{J} = \boldsymbol{j}_1 + \boldsymbol{j}_2$. Determine using `ClebschGordan[{j1,m1},{j2,m2},{J,M}]` in Mathematica the wavefunction for the state $J = 3/2, M = 1/2$ in terms of the eigenstates of j_1^2, j_{1z}, j_2^2 en j_{2z}.

Exercise 17.3

(a) Determine the multiplets, their spectroscopic terms and their energy ordering for all $(np)^x$ configurations.

(b) Similar for $(np)(n'p)$ with $n \neq n'$. Compare the levels with those for Carbon.

Exercise 17.4

Construct the possible spectroscopic terms of a Barium atom in a $(6p)(5d)$ state. Give the degeneracy of each of the terms and heck that there are (as expected) 60 states. Use the Hund rules to order the states.

Exercise 17.5

We look at two spin 1/2 particles for which the spin operators can be described using the Pauli matrices. For the two-particle states we consider the (direct) product basis $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$.

(a) Construct explicitly the (4×4) matrices $\boldsymbol{S}_1 = \boldsymbol{S}_1 \otimes \hat{I}_2$ and $\boldsymbol{S}_2 = \hat{I}_1 \otimes \boldsymbol{S}_2$ in the two-particle space.

(b) Construct the matrices $\boldsymbol{S} = \boldsymbol{S}_1 + \boldsymbol{S}_2$.

(c) Construct the matrix $\boldsymbol{S}^2$.

(d) Show that S_z and $\boldsymbol{S}^2$ commute.

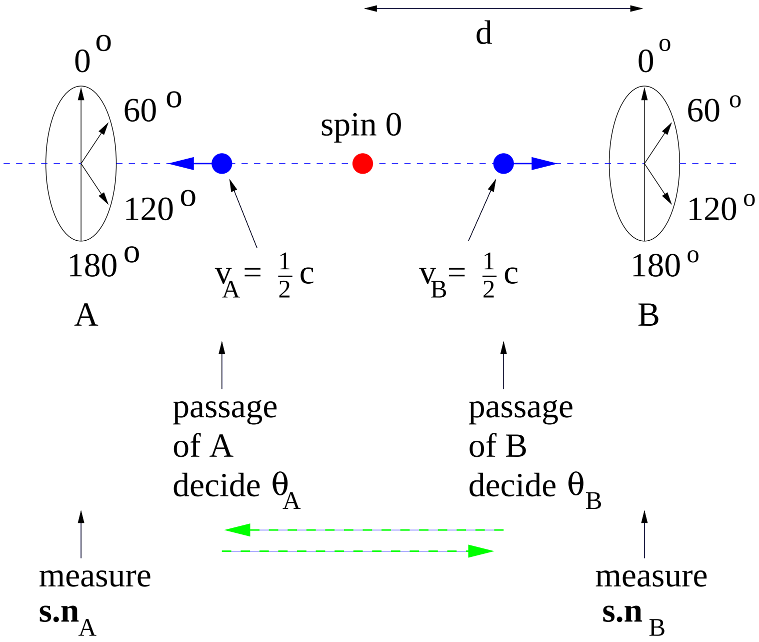
(e) Determine the eigenvalues of S_z and $\boldsymbol{S}^2$ and the (common) set of eigenstates.

(f) Check that the result agrees with the table of Clebsch-Gordan coefficients for $1/2 \otimes 1/2 = 0 \oplus 1$.

18 The EPR experiment

18.1 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[6].



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:

$\lvert\theta_A - \theta_B\rvert =$	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

---

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

18.2 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 encounter a Stern-Gerlach apparatus under a given angle θ_A. E.g.

$$\begin{array}{lll} \text{Event 1:} & \text{memory\_A} = (+-+) & \text{memory\_B} = (-+-) \\ \text{Event 2:} & \text{memory\_A} = (++-) & \text{memory\_B} = (--+) \end{array}$$

etc. For instance in the first example the prescription tells A that if $\theta_A = 0^\circ$, then a spin measurement yields $+\hbar/2$, if $\theta_A = 60^\circ$, then a spin measurement yields $-\hbar/2$, while if $\theta_A = 120^\circ$, 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.

$$\begin{aligned} P(\theta_A = 0^\circ, +; \theta_B = 120^\circ, +) &= \sum_{\sigma=-\tau} f(+\sigma-; -\tau+) \\ &= f(++-;--+) \ + \ f(+--;-++) \end{aligned} \tag{331}$$

$$P(\theta_A = 60^\circ, +; \theta_B = 120^\circ, +) = f(++-;--+) \ + \ \underbrace{f(-+-;+-+)}_{\geq 0} \tag{332}$$

$$P(\theta_A = 0^\circ, +; \theta_B = 60^\circ, +) = \underbrace{f(+-+;-+-)}_{\geq 0} + f(+--;-++), \tag{333}$$

and hence we must have in a realistic theory

$$P(\theta_A = 60^\circ, +; \theta_B = 120^\circ, +) + P(\theta_A = 0^\circ, +; \theta_B = 60^\circ, +) \geq P(\theta_A = 0^\circ, +; \theta_B = 120^\circ, +), \tag{334}$$

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.

18.3 The quantum-mechanical explanation!

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

$$|AB\rangle = \frac{1}{\sqrt{2}} \left(|A\uparrow\rangle \otimes |B\downarrow\rangle - |A\downarrow\rangle \otimes |B\uparrow\rangle \right) \tag{335}$$

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

$$P(\theta_A = 0^\circ, +; \theta_B, +) = \left| \langle A\uparrow|A\uparrow\rangle \, \langle \theta_B, + |B\downarrow\rangle \right|^2 = \sin^2(\theta_B/2). \tag{336}$$

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

18.4 Quantum computing: Qubits and juggling with them

While a classical computer uses bits (with two possible values, 0 and 1) to represent numbers, a quantum computer would employ two quantum states, $|0\rangle$ or $|1\rangle$ to store information. These are called *Qubits.* These could be the two spin states of a spin 1/2 particle, but (more practical) could be two states for a trapped ion, e.g. in combining the spin of an electron (S = 1/2) with the spin of the atomic nucleus (I) one gets two states with a combined spin $F = I \pm 1/2$. These states have slightly different energy because of the hyperfine interaction (see next section) and could represent our two possible states $|0\rangle$ and $|1\rangle$. In general a quantum state can be in a superposition of these two states, which omitting an overall phase can be written explicitly or as a 2-dimensional state vector,

$$|\text{qubit}\rangle = \cos\left(\tfrac{\theta}{2}\right)|0\rangle + \mathrm{e}^{\mathrm{i}\phi}\,\sin\left(\tfrac{\theta}{2}\right)|1\rangle = \left(\begin{array}{c} \cos\left(\frac{\theta}{2}\right) \\ \\ e^{i\phi}\,\sin\left(\frac{\theta}{2}\right)\end{array}\right). \tag{337}$$

It is parametrized with angles (θ,ϕ), which run over the socalled *Bloch sphere.* The information content, however, is the same as a classical bit. A measurement (of say the energy) yields one or the other state. Nevertheless, in quantum computing one often juggles with linear combination of bits and then the representation as an arrow pointing from the center to the surface of the Bloch sphere is convenient. For instance $|0\rangle$ and $|1\rangle$ represents arrows pointing to the North and South pole of the Bloch sphere. Flipping the states is known as the NOT (also called FLIP or SWAP) operation $\boldsymbol{X}$,

$$\boldsymbol{X}|0\rangle = |1\rangle, \qquad \boldsymbol{X}|1\rangle = |0\rangle,$$

(the name NOT should be obvious), which is represented as a (unitary) matrix in our 2-dimensional space,

$$\boldsymbol{X} = \left(\begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array}\right), \tag{338}$$

represented by a 180 degree rotation around the x (or y)-axis for the vector on the Bloch sphere.

One of the most important operations on a single qubit is the Hadamard operation,

$$\boldsymbol{H} == \frac{1}{\sqrt{2}}\left(\begin{array}{cc} 1 & 1 \\ 1 & -1 \end{array}\right), \tag{339}$$

which produces from the single qubits state a linear combination of the two states, corresponding to a 90 degree rotation on the Bloch sphere. It is relatively easy to realize such an operation. For instance prepare a spin 1/2 particle with spin in the x-direction when the basic qubits correspond to the spin states along the z-direction. Note that applying the Hadamard twice gives a switch, $\boldsymbol{H}^2 = \boldsymbol{X}$. One also writes $\boldsymbol{H} = \sqrt{\boldsymbol{X}}$.

There are a some other useful operators at this one-qubit level, such as the zero and unit operators,

$$\boldsymbol{O} = \left(\begin{array}{cc} 0 & 0 \\ 0 & 0 \end{array}\right) \quad \text{and} \quad \boldsymbol{I} = \left(\begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array}\right),$$

and the projection operators (satisfying $\boldsymbol{P}^2 = \boldsymbol{P}$),

$$\boldsymbol{N} = \left(\begin{array}{cc} 0 & 0 \\ 0 & 1 \end{array}\right) \quad \text{and} \quad \overline{\boldsymbol{N}} = \left(\begin{array}{cc} 1 & 0 \\ 0 & 0 \end{array}\right),$$

which satisfy

$$\boldsymbol{N}^2 = \boldsymbol{N}, \quad \overline{\boldsymbol{N}}^2 = \overline{\boldsymbol{N}}, \quad \boldsymbol{N}\overline{\boldsymbol{N}} = \overline{\boldsymbol{N}}\boldsymbol{N} = \boldsymbol{O}, \quad \boldsymbol{N} + \overline{\boldsymbol{N}} = \boldsymbol{I}.$$

An interesting operator is

$$\boldsymbol{Z} = \boldsymbol{N} - \overline{\boldsymbol{N}} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

which leaves $|0\rangle$ unmodified and switches the sign of $|1\rangle$. We note that the operators $\boldsymbol{N}$, $\overline{\boldsymbol{N}}$ and $\boldsymbol{Z}$ cannot be physical operators in our quantum computer because they multiply a physical state with the number zero or the number -1. They turn out to be useful, however, in manipulations in qubit-space, representing the effect on one qubit that is a consequence of a physical manipulations on two or three qubits. On the Bloch sphere $\boldsymbol{Z}$ corresponds to a rotation over π around the z-axis. Adding also the combined NOT and $\boldsymbol{Z}$ operator, we have

$$\boldsymbol{Y} = \boldsymbol{Z}\boldsymbol{X} = -\boldsymbol{X}\boldsymbol{Z} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}.$$

The operators $\boldsymbol{X}$, $\boldsymbol{Y}$ and $\boldsymbol{Z}$ are up to a factor for $\boldsymbol{Y}$ just the familiar Pauli matrices, $\boldsymbol{X} \leftrightarrow \sigma_x$, $\boldsymbol{Y} \leftrightarrow i\sigma_y$ and $\boldsymbol{Z} \leftrightarrow \sigma_z$. We also have $\boldsymbol{X}^2 = -\boldsymbol{Y}^2 = \boldsymbol{Z}^2 = \boldsymbol{I}$. In quantum computation one works with specific physical actions, such as transitions between the levels of the trapped ions, that act as quantum logic gates (unitary transformations) on one or on a subset of the qubits.

18.5 Entanglement

Considering a sequence of trapped ions one can have (multi-particle) states $|000\rangle$, $|010\rangle$, etc. There are four two-particle states, $|00\rangle$, $|01\rangle$, $|10\rangle$ and $|11\rangle$, for which we use (interchangeable) notations like $|00\rangle = |0\rangle|0\rangle = |0\rangle \otimes |0\rangle$, etc. (see the pre-knowledge discussion in section 17). Having more qubits, one often operates on one or two of the qubits out of a larger multi-qubit configuration. Then it is useful to specify e.g. $|x\rangle_3$ or $|xy\rangle_{12}$ as subsets of a larger chain.

Having more qubits, it is now possible to have two-particle states of the type

$$|\psi\rangle \propto |01\rangle - |10\rangle, \tag{340}$$

(in complete analogy with the spin 0 state $\big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\big)/\sqrt{2}$). Although the basis multi-particle states are (direct) products, the state in Eq. 340 has the property that it cannot be written as a simple product of single-particle states,

$$|\psi\rangle \neq |\psi_1\rangle|\psi_2\rangle, \tag{341}$$

even if one allows

$$|\psi_1\rangle|\psi_2\rangle = \big(a|0\rangle_1 + b|1\rangle_1\big)\big(c|0\rangle_2 + d|1\rangle_2\big) = ac|00\rangle + ad|01\rangle + bc|10\rangle + bd|11\rangle. \tag{342}$$

Such states are called *entangled*. In the previous chapter we have seen that entangled states have different correlations built in as compared to uncorrelated (direct) product states (which could just be classical objects). This is directly connected to the measuring process in quantum mechanics, which projects onto specific eigenstates of the analyzer.

For two-qubit states, the operators can in general be written as a superposition of direct products of single-particle operators, denoted (interchangeable) as $\boldsymbol{A}_{12} = \boldsymbol{A}_1 \otimes \boldsymbol{A}_2 = \boldsymbol{A}_1\boldsymbol{A}_2 = \boldsymbol{A}_2\boldsymbol{A}_1$, operating according to the direct product prescription $\boldsymbol{A}_{12}|xy\rangle = \boldsymbol{A}_1|x\rangle \otimes \boldsymbol{A}_2|y\rangle$. In the two-qubit space such operators can be written as 4×4 matrices with as standard choice for the basis $|00\rangle$, $|01\rangle$, $|10\rangle$, $|11\rangle$.

Note that a Hadamard operation on one qubit produces at the two-qubit level an entangled state, $\boldsymbol{H}_1|00\rangle \propto |01\rangle + |11\rangle$. (Note that $\boldsymbol{H}_1$ is actually shorthand for $\boldsymbol{H}_1 \otimes \boldsymbol{I}_2$). The operation brings the two-qubit system in an entangled state, in which the information is no longer encoded in individual registers as for a classical computer.

The SWAP operation at the two-qubit level leaves $|00\rangle$ and $|11\rangle$ the same and interchanges $|01\rangle$ and $|10\rangle$. It can be written as a 4×4 matrix, but it can also be expressed in a combination of single-qubit operators,

$$\boldsymbol{S}_{12} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \boldsymbol{N}_1\boldsymbol{N}_2 + \overline{\boldsymbol{N}}_1\overline{\boldsymbol{N}}_2 + \big(\boldsymbol{X}_1\boldsymbol{X}_2\big)\big(\boldsymbol{N}_1\overline{\boldsymbol{N}}_2 + \overline{\boldsymbol{N}}_1\boldsymbol{N}_2\big). \tag{343}$$

One of the most important operations for two qubits is the Controlled-NOT or CNOT operation, which changes the second qubit (target-qubit), depending on the state of the first qubit (control-qubit). Thus

$$\boldsymbol{C}_{12} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} = \overline{\boldsymbol{N}}_1 + \boldsymbol{X}_2\boldsymbol{N}_1. \tag{344}$$

A CNOT operation can be achieved by a relatively straightforward physical operation that employs small energy shifts of the trapped atoms because of their interactions with the surrounding atoms.

The essence of quantum computing is the enhancement of entanglement. By storing the information at a given time in an entangled state over 10 registers enables in essence calculation on 2^{10} states at the same time. Of course, in spite of all information stored in the system one can only do one read-out, which in the case of entanglement for a given register, moreover, may yield $|0\rangle$ or $|1\rangle$ with certain probabilities. This puts high demands on the algorithms, which should make sure that finally the wanted information is again available in (more or less) de-entangled registers.

19 Bound state perturbation theory

19.1 Basic treatment

Perturbation theory is used to obtain in a systematic way a solution for a hamiltonian $H = H_0 + \lambda V$ in the form of an expansion in the (small) parameter λ, assuming the solutions of H_0 are known, $(H_0 - E_n^{(0)})\,|\phi_n\rangle = 0$. One inserts expansions for the energy and the solution of the form

$$E_n = E_n^{(0)} + \lambda\, E_n^{(1)} + \lambda^2\, E_n^{(2)} + \ldots, \tag{345}$$

$$|\psi_n\rangle = |\phi_n\rangle + \lambda\,|\psi_n^{(1)}\rangle, \tag{346}$$

into the Schrödinger equation $(H - E_n)|\psi_n\rangle = 0$,

$$\big(H_0 + \lambda\, V\big)\big(|\phi_n\rangle + \lambda\,|\psi_n^{(1)}\rangle + \ldots\big) = \big(E_n^{(0)} + \lambda\, E_n^{(1)} + \ldots\big)\big(|\phi_n\rangle + \lambda\,|\psi_n^{(1)}\rangle + \ldots\big). \tag{347}$$

After ordering the terms according to the power of λ, one finds at zeroth order the unperturbed Schrödinger equation for $|\phi_n\rangle$ and at first order

$$\lambda\, V|\phi_n\rangle + \lambda\, H_0|\psi_n^{(1)}\rangle = \lambda\, E_n^{(1)}|\phi_n\rangle + \lambda\, E_n^{(0)}|\psi_n^{(1)}\rangle. \tag{348}$$

Realizing that the unperturbed solutions form a complete set we take the scalar product with $\langle\phi_n|$ and with $\langle\phi_m|$ for $m \neq n$, yielding

$$\lambda\, E_n^{(1)} = \langle\phi_n|\lambda\, V|\phi_n\rangle, \tag{349}$$

$$\lambda\big(E_n^{(0)} - E_m^{(0)}\big)\langle\phi_m|\psi_n^{(1)}\rangle = \langle\phi_m|\lambda\, V|\phi_n\rangle \quad (\text{for } m \neq n). \tag{350}$$

To obtain the first equation we have assumed that $\psi_n^{(1)}\rangle$ can be choosen orthogonal to $|\phi_n\rangle$ (thus $\langle\phi_n|\rangle\psi_n^{(1)}\rangle = 0$). This can be done without loss of generality. It may be necessary to renormalize the final result, because we have more or less arbitrary set the coefficient of $|\phi_n\rangle$ equalt to one. The first equation gives the first order shift in the energy $\Delta E = E - E_n = \lambda\, E_n^{(1)}$, the second gives the correction in the wave function. Summarizing,

$$E_n^{(1)} = \langle\phi_n|V|\phi_n = V_{nn}, \tag{351}$$

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n} |\phi_m\rangle\, \frac{\langle\phi_m|V|\phi_n\rangle}{E_n^{(0)} - E_m^{(0)}} = \sum_{m\neq n} |\phi_m\rangle\, \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}}. \tag{352}$$

The latter result can be written down *only* for the case that the unperturbed state $|\phi_n\rangle$ is nondegenerate.

The second order results involve the λ^2 terms of Eq. 347, giving

$$H_0|\psi_n^{(2)}\rangle + V|\psi_n^{(1)}\rangle = E_n^{(0)}|\psi_n^{(2)}\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle + E_n^{(2)}|\phi_n\rangle. \tag{353}$$

Taking the scalar product with $\langle\phi_n|$ gives the result

$$E_n^{(2)} = \langle\phi_n|V|\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{V_{nm}\,V_{mn}}{E_n^{(0)} - E_m^{(0)}}. \tag{354}$$

Perturbation theory is very useful if the first-order shift in the energies is small, to be more precise if $|\langle\phi_m|\lambda\, V|\phi_n\rangle| \ll |E_n^{(0)} - E_m^{(0)}|$ for all $m \neq n$. In principle the expressions have been written down for discrete spectra, but for bound states we can generalize

$$\sum_{m\neq n} \Rightarrow \sum_{m\neq n} + \int_0^\infty dE\,\rho(E), \tag{355}$$

where the integral covers the continuum spectrum in which $\rho(E)\,dE$ is the number of states in an energy interval dE around E.

19.2 Perturbation theory for degenerate states

In many applications we will encounter the situation that the energy levels in the unperturbed hamiltonian will be degenrate, in which case the step from Eq. 350 to 352 cannot be made. Eq. 350, however, also tells us how to proceed. Make sure that the states $|\phi_{n1}\rangle$, ..., $|\phi_{ns}\rangle$ which are degenerate with respect to H_0 are choosen to be eigenstates of the perturbation λV. In that case we can choose the wave function corrections orthogonal to all $|\phi_{nr}\rangle$ and we have $\langle\phi_{ni}|\lambda V|\phi_{nj}\rangle = 0$. The result is that we get instead of Eq. 352 the result

$$|\psi_n^{(1)}\rangle = \sum_{E_m^{(0)} \neq E_n^{(0)}} |\phi_m\rangle \, \frac{\langle\phi_m|V|\phi_n\rangle}{E_n^{(0)} - E_m^{(0)}}. \tag{356}$$

In practice we often look for a suitable set of states for which both the unperturbed hamiltonian and the perturbation potential are diagonal by looking for a relevant set of compatible operators. In worst case one can ressort to a brute force diagonalisation of the perturbation potential.

19.3 Applications

Fine structure in hydrogen: the mass correction

In the hydrogen atom there are a number of additional terms in the hamiltonian that can be attributed to relativistic corrections,

$$H = H_0 + H_{\text{mass}} + H_{\text{Foldy}} + H_{\text{so}} \tag{357}$$

The first term is a correction coming from the difference of the relativistic and nonrelativistic kinetic energies,

$$H_{\text{mass}} = \sqrt{\boldsymbol{p}^2 c^2 + m^2 c^4} - mc^2 - \frac{\boldsymbol{p}^2}{2m} \approx -\frac{\boldsymbol{p}^4}{8m^3c^2}. \tag{358}$$

Including this correction, the operators $\boldsymbol{\ell}^2$ and ℓ_z still remain compatible with the hamiltonian, but the radial dependence now will be modified. However in *first order perturbation theory* one obtains an accurate estimate of the energy shifts by calculating the expectation value of the correction. We here just state the result (treated in many quantum mechanics books),

$$\Delta E_{\text{mass}}(n\ell) = \langle n\ell m\ldots| - \frac{\boldsymbol{p}^4}{8m^3c^2}|n\ell m\ldots\rangle = -\alpha^2\,\frac{R_\infty}{n^3}\left(\frac{1}{\ell+\frac{1}{2}} - \frac{3}{4n}\right). \tag{359}$$

Fine structure in hydrogen: the spin-orbit interaction

Another interaction term arises because of the interaction of the spin with the induced magnetic field by the orbital motion. It can be up to a factor 2 be derived with classical arguments, but a proper derivation requires the use of the relativistic Dirac equation for the electron. The result for a particle in a central potential is

$$H_{\text{so}} = \frac{1}{2m^2c^2}\,\frac{1}{r}\,\frac{dV_c}{dr}\,\boldsymbol{\ell}\cdot\boldsymbol{s}. \tag{360}$$

When applying perturbation theory for this term one must be careful. One cannot simply calculate the expectation value between hydrogen states $|n\ell s m_\ell m_s\rangle$. Since the level is $2(2\ell+1)$-fold degenerate the perturbation mixes these degenerate states. Application of perturbation theory requires a reordering of these states, such that they are compatible with the perturbation. Instead of the brute force way of diagonalizing the matrix $\langle n\ell s m_\ell' m_s'|H_{\text{so}}|n\ell s m_\ell m_s\rangle$, there is a smarter way. By rewriting

$$\boldsymbol{\ell}\cdot\boldsymbol{s} = \frac{1}{2}\left[\boldsymbol{j}^2 - \boldsymbol{\ell}^2 - \boldsymbol{s}^2\right],$$

one sees that the operators $\boldsymbol{\ell}^2$, $\boldsymbol{s}^2$, $\boldsymbol{j}^2$ and j_z (which from the theory of addition of angular momenta are known to be compatible with each other) are also compatible with the hamiltonian. This is not true for the set $\boldsymbol{\ell}^2$, $\boldsymbol{s}^2$, ℓ_z and s_z. Hence if we use states $|n\ell s j m\rangle$, the correction term has no off-diagonal elements, hence does (for given ℓ and s not mix the unperturbed degenerate states and the splitting for the correct combinations of states is directly found as

$$\begin{aligned}\Delta E_{\rm so}(n\ell s j m) &= \frac{1}{2m^2c^2}\langle n\ell s j m|\frac{1}{r}\,\frac{dV_c}{dr}\,\boldsymbol{\ell}\cdot\boldsymbol{s}|n\ell s j m\rangle \\ &= \frac{e^2\,\hbar^2}{32\pi\epsilon_0\,m^2c^2}\,\langle n\ell|\frac{1}{r^3}|n\ell\rangle\;[j(j+1)-\ell(\ell+1)-s(s+1)] \\ &= \frac{e^2\,\hbar^2}{32\pi\epsilon_0\,m^2c^2}\,\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{a_0^3\,n^3\,\ell(\ell+1)(\ell+\frac{1}{2})} \qquad (361)\end{aligned}$$

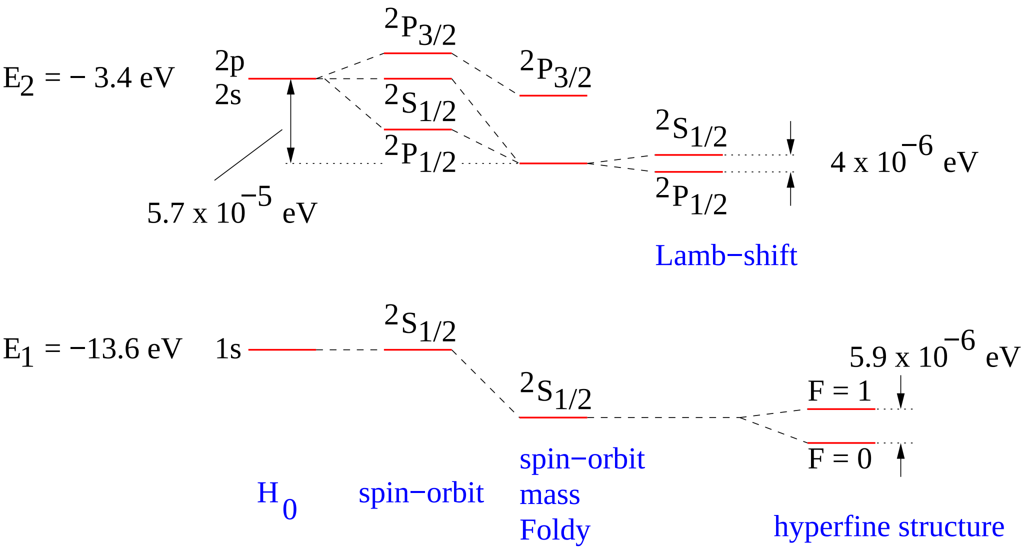
We thus must couple ℓ and s to j-eigenstates. For one electron with a given $\ell \neq 0$ there are two possibilities for j, namely $j = \ell \pm \frac{1}{2}$ giving for $\ell \neq 0$

$$\Delta E_{\rm so}(n\ell j) = \alpha^2\,\frac{R_\infty}{n^3}\left(\frac{1}{\ell+\frac{1}{2}} - \frac{1}{j+\frac{1}{2}}\right) \qquad (362)$$

and for the combined result

$$\Delta E_{\rm mass\ +\ so} = -\alpha^2\,\frac{R_\infty}{n^3}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right) \qquad (363)$$

In the Hydrogen atom one also has the Foldy term, which is a relativistic correction proportional to $\delta^3(\boldsymbol{r})$ and thus only affects s-waves. It makes the above equation valid also for s-waves. Schematically (not on scale) one has the following fine structure in the hydrogen spectrum



The various terms cause shifts in the order of 10^{-4} eV, giving within a orbit characterized by the principal quantum number n states with well-defined j-values. We denote such a level with a *term symbol*, for hydrogen

$$(n\ell)\;^{(2S+1)}L_J$$

where $(n\ell)$ indicates the spatial part of the electron wave function, $2S+1$ is the total spin multiplicity and L is the total orbital angular momentum of the electrons (using notation $S, P, D, \ldots$ for $L = 0, 1, 2, \ldots$).

In this specific case of hydrogen with just one electron $S = 1/2$ and the multiplicity is always 2 while $L = \ell$. The splitting of the ${}^2S_{1/2}$ and ${}^2P_{1/2}$ is about 4×10^{-6} eV produces a splitting of the Lyman α line. Also transitions between both levels are possible via an E1 transition with frequency of about 1 GHz.

Fine structure in hydrogen: the hyperfine splitting

The hyperfine structure in hydrogen is due to the interaction of the magnetic moments of electron and nucleus. Also the proton has a magnetic moment, which induces a magnetic dipole field felt by the electron and vice versa. It produces an interaction term, which for s-waves is of the form

$$V_{ss} = \frac{1}{6\pi\epsilon_0\, c^2}\, \boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_p\, \boldsymbol{\nabla}^2\, \frac{1}{r}. \tag{364}$$

We know that $\boldsymbol{\mu}_e = g_e\,(e/m_e)\,\boldsymbol{S}$ and $\boldsymbol{\mu}_p = g_p\,(e/M_p)\,\boldsymbol{I}$ (where we use the in atomic physics conventional notation $\boldsymbol{I}$ for the nuclear spin). The splitting thus is proportional to

$$\Delta E_{ss} \propto g_e\, g_p\, \langle|\boldsymbol{S}\cdot\boldsymbol{I}|\rangle = \frac{1}{2}\, g_e\, g_p\, \hbar^2\, \left[F(+F1) - S(S+1) - I(I+1)\right]. \tag{365}$$

The proper eigenstates are labeled by eigenstates for the angular momentum operators F^2 and F_z, where $\boldsymbol{F} = \boldsymbol{S} + \boldsymbol{I}$. For normal hydrogen in the ground state ($I = 1/2$), it produces two states with $F = 0$ (para-) and $F = 1$ (ortho-hydrogen). The splitting is much smaller than the fine structure. For the $(1s)\,{}^2S_{1/2}$ level in hydrogen the splitting is 5.9×10^{-6} eV (see figure in previous section), corresponding to a transition frequency $\nu_{hf} = 1.42$ GHz or a wavelength of 21 cm. Although the radiative transition is heavily suppressed (it is certainly not an electric dipole transition!) it plays a very important role in radio astronomy. It traces the abundant occurence of hydrogen in the universe not in the least since the 21 cm wavelength is not strongly attenuated by interstellar dust.

Refinements for Helium

Including the ee-interaction the hamiltonian for 2 electrons in an atom is

$$H(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{p}_1, \boldsymbol{p}_2) = \underbrace{\left(-\frac{\hbar^2}{2m}\,\boldsymbol{\nabla}_1^2 - \frac{Ze^2}{4\pi\epsilon_0\, r_1}\right)}_{H_1} + \underbrace{\left(-\frac{\hbar^2}{2m}\,\boldsymbol{\nabla}_2^2 - \frac{Ze^2}{4\pi\epsilon_0\, r_2}\right)}_{H_2} + \underbrace{\frac{e^2}{4\pi\epsilon_0\, |\boldsymbol{r}_1 - \boldsymbol{r}_2|}}_{H_{12}},$$

which does not factorize because of the electron-electron interaction term. A way to account for the ee-interaction is by treating it as a perturbation on the result in the previous section. In perturbation theory the shift of the lowest level in the zeroth order approximation for Helium, the $(1s)^2\,{}^1S_0$ multiplet, is simply given by the evaluating the ee-interaction term between the unperturbed wave function, which can straightforwardly be calculated

$$\Delta E_{\rm gs} = \int d^3r_1\, d^3r_2\; |\phi_{1s}(\boldsymbol{r}_1)|^2\, |\phi_{1s}(\boldsymbol{r}_1)|^2\, \frac{e^2}{4\pi\epsilon_0 |\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \frac{5}{4}\, Z\, R_\infty, \tag{366}$$

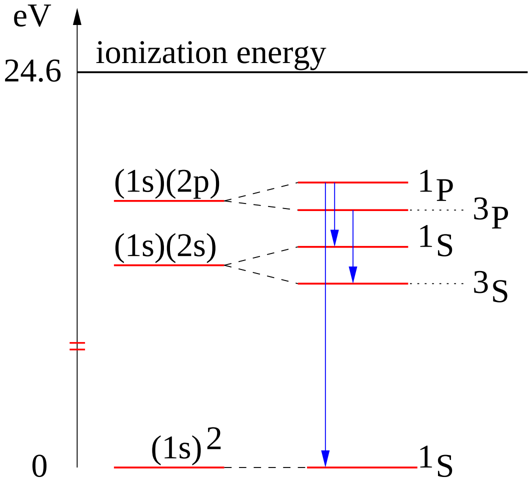
giving as estimate for the binding of the ${}^1S_0$ level $E = \left(-2Z^2 + \frac{5}{4}\,Z\right) R_\infty$, which for $Z = 2$ gives $E \approx -5.5\, R_\infty$, considerably higher than the previous result $E^{(0)} = -8$ eV and not bad as compared to the experimental value $E_{\rm gs} = -5.81\, R_\infty$.

For the next multiplets one has a spatially symmetric or antisymmetric wave function of the form $\psi = \psi_1 \pm \psi_2$, the sign depending on the spin wave function and one obtains for the expectation value of the hamiltonian,

$$\begin{aligned}\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} &= \frac{\langle\psi_1 \pm \psi_2|H_1 + H_2 + H_{12}|\psi_1 \pm \psi_2\rangle}{\langle\psi_1 \pm \psi_2|\psi_1 \pm \psi_2\rangle} \\ &= E_1 + E_2 + \frac{C \pm K}{1 \pm S}, \qquad (367)\end{aligned}$$

where

$$\begin{aligned}&\langle\psi_1|\psi_1\rangle = \langle\psi_2|\psi_2\rangle = 1 \quad \text{(assumed normalized)},\\ &\langle\psi_1|H_i|\psi_1\rangle = E_i \qquad \text{(i = 1,2)},\\ &\langle\psi_1|\psi_2\rangle = \langle\psi_2|\psi_1\rangle = S \qquad \text{(overlap integral)},\\ &\langle\psi_1|H_i|\psi_2\rangle = \langle\psi_2|H_i|\psi_2\rangle = E_i\, S \qquad \text{(i = 1,2)},\\ &\langle\psi_1|H_{12}|\psi_1\rangle = \langle\psi_2|H_{12}|\psi_2\rangle = C \qquad \text{(Coulomb integral)},\\ &\langle\psi_1|H_{12}|\psi_2\rangle = \langle\psi_2|H_{12}|\psi_1\rangle = K \qquad \text{(exchange integral)}.\end{aligned}$$



Looking at the $(1s)(2p)$ and $(1s)(2s)$ configurations and the shifts in perturbation theory, the exchange integral K turns out to be important yielding the lowest energy for the antisymmetric spatial wave function. These are combined with $S = 1$. For the excited levels of Helium the $S = 1$ (ortho-Helium) multiplets have the lowest energies. The groundstate configuration of Helium only has $S = 0$ (para-Helium). In the figure some dipole transitions have been indicated.

The fine structure of atoms

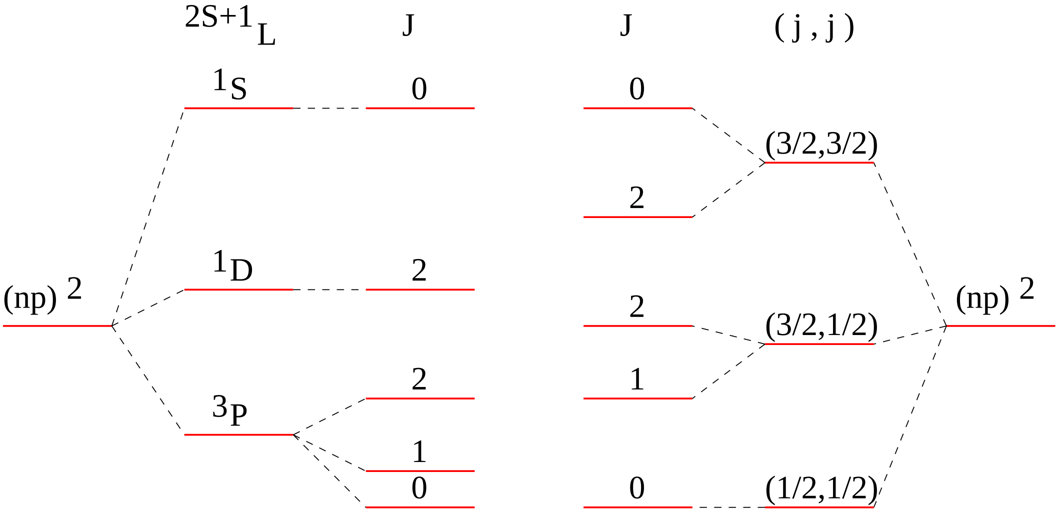
When combining angular momenta, we discussed the multiplets forming the fine structure in atoms. For not too heavy atoms, the energies for the multiplets turn out to be described well by a spin-orbit interaction of the form

$$H_{\text{so}} = A(L,S)\,\boldsymbol{L}\cdot\boldsymbol{S}, \qquad (368)$$

with a strenght A depending on the multiplet, coming among others from the radial dependence of the basic interaction. The spin-orbit interaction splits states with different J-values, leading to ${}^{2S+1}L_J$ multiplets and a magnitude for the splitting being given by

$$\Delta E(LSJM) = \frac{1}{2}\,A\hbar^2\left[J(J+1) - L(L+1) - S(S+1)\right]. \qquad (369)$$

An example of the splitting of the three terms for an $(np)^2$ configuration is given below.



Note that the average (beware of degeneracy) of a multiplet gives the energy of the multiplet without the spin-orbit interaction. The pattern of levels can in principle be obtained from atomic spectra. The use of magnetic fields is helpful to determine the degeneracy of the levels. But already the spin-orbit splittings contains interesting patterns, such as

$$r = \frac{E(^{2S+1}L_J) - E(^{2S+1}L_{J-1})}{E(^{2S+1}L_{J-1}) - E(^{2S+1}L_{J-2})} = \frac{J}{J-1}, \tag{370}$$

e.g. for the ratio $(E(^3P_2) - E(^3P_1))/(E(^3P_1) - E(^3P_0))$ one expects $r = 2$ if LS-coupling describes the fine structure. For Carbon the actual ratio is 1.65, for Silicium (Si) it is 1.89, but for a heavy atom as lead (Pb) the result is just 0.36, indicating a different type of fine structure. A different scheme is the jj-scheme in which first the orbital angular momenta and spins of the electrons are coupled, which in turn are combined into J-values, illustrated in the figure for the $(np)^2$ configuration. Note that coupling two identical j-values of the electrons, one needs to account for the symmetry of the wave function. The wave function for the maximal $J = 2j$ is symmetric, for the next lower J it is antisymmetric, then again symmetric, etc. This explains the J-values in the jj-coupling scheme. In the final result the same J-values must appear, but note that the actual wave functions are different.

Exercises

Exercise 19.1

(a) Include spin-orbit interactions to find the possible J-values in the $(6p)(5d)$ configuration of a Barium atom (see Exercise 17.3).

(b) Give the corresponding construction of allowed J-values in the jj-coupling scheme.

Exercise 19.2

Consider the hamiltonian H for the Hydrogen atom given by

$$H = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} .$$

with eigenstates ϕ_{nlm}.

a. What is the hamiltonian if the atom is in an external electric field with strength $\boldsymbol{E} = E\,\hat{\boldsymbol{z}}$?

b. Explain that the first order correction in the field $\boldsymbol{E}$ does not affect the energy of the ground state ($n = 1$).

c. Determine the first order correction for the energy of the $n = 2$ levels in the external electric field. Give a level scheme in which you indicate the zeroth order results of the $n = 2$ levels and their splitting. [Hint: $\langle\phi_{210}|z|\phi_{200}\rangle = -3\,a_0$.]

Exercise 19.3

Prove the relation

$$r = \frac{E(^{2S+1}L_J) - E(^{2S+1}L_{J-1})}{E(^{2S+1}L_{J-1}) - E(^{2S+1}L_{J-2})} = \frac{J}{J-1}.$$

20 Magnetic effects in atoms and the electron spin

20.1 The Zeeman effect

Interaction of orbital angular momentum with magnetic field

In a magnetic field an additional interaction is added to the hamiltonian,

$$H = \underbrace{-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \frac{Ze^2}{4\pi\epsilon_0\, r}}_{H_0} + V_{\rm mag}, \tag{371}$$

where $V_{\rm mag} = -\boldsymbol{\mu}\cdot B$. Neglecting spin, the magnetic moment of a particle in orbit is given by

$$\boldsymbol{\mu}_\ell = -g_\ell\,\frac{e}{2m}\,\boldsymbol{\ell} \tag{372}$$

with $g_\ell = 1$. What are the eigenfunctions and eigenvalues (energies) of this new hamiltonian. For this it is useful to find as many as possible commuting operators. Commuting operators are H, $\boldsymbol{\ell}^2$, ℓ_z (and, although overcomplete, the parity operator). However, the term

$$V_{\rm mag} = \frac{e}{2m}\,\boldsymbol{\ell}\cdot\boldsymbol{B},$$

implies that one only can have ℓ_z as an operator compatible with H if the z-axis is chosen along $\boldsymbol{B}$, i.e. $\boldsymbol{B} = B\,\hat{\boldsymbol{z}}$. In that case it is easy to convince oneself that the eigenfunctions are still the hydrogen wave functions, while the energies are shifted over an amount

$$\Delta E_{n\ell m_\ell} = \langle n\ell m_\ell|\frac{eB}{2m}\,\ell_z|n\ell m_\ell\rangle = m_\ell\,\mu_B B, \tag{373}$$

where

$$\mu_B = \frac{e\hbar}{2m} = \frac{1}{2}\,e\,c\,\frac{\hbar}{mc} \approx 5.8\times 10^{-5}\ \text{eV/T} \tag{374}$$

is the Bohr magneton.

Interaction of electron spin with magnetic field

For a proper description of an electron, one needs to specify in addition to $\psi(\boldsymbol{r},t)$ a spin wave function. For electrons with spin 1/2 one can resort to a description with two-component wave functions, where the spin operators are given by matrices, $\boldsymbol{s} = \frac{1}{2}\,\hbar\boldsymbol{\sigma}$ where $\boldsymbol{\sigma}$ are the three *Pauli matrices*. Just as the orbital angular momentum, the spin gives in a magnetic field rise to an interaction term in the hamiltonian.

$$V_{\rm mag} = -\boldsymbol{\mu}_s\cdot\boldsymbol{B}, \tag{375}$$

with

$$\boldsymbol{\mu}_s = -g_s\,\frac{e}{2m}\,\boldsymbol{s} = -g_s\,\frac{e\hbar}{m}\,\boldsymbol{\sigma}. \tag{376}$$

The g-factor for the spin of the electron is $g_s \approx 2$. Actually the deviation from 2 is due to subtle but calculable effects in quantum electrodynamics, $g_e - 2 = \alpha/\pi + \ldots \approx 0.00232$. If the interaction of the spin with the magnetic field is the only interaction (e.g. for s-waves), the result of the interaction term is a simple shift in the energies for the states, that now include also spin quantum numbers.

The Zeeman effect in many-electron atoms

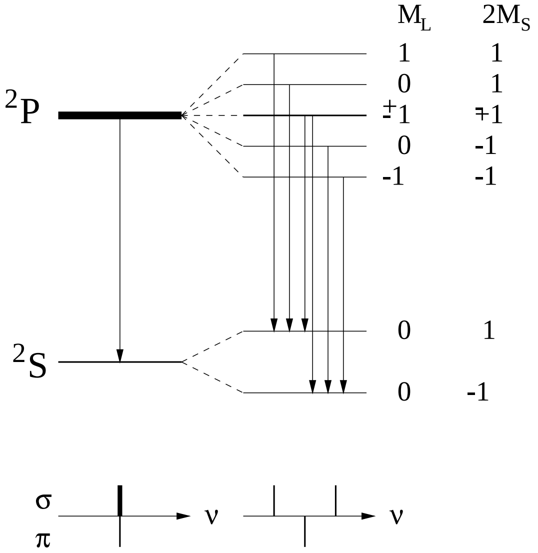
In general a ${}^{2S+1}L$ level in a magnetic field is split by an interaction term

$$V_{\rm mag} = -\boldsymbol{\mu}\cdot\boldsymbol{B}, \tag{377}$$

where $\boldsymbol{\mu} = -\mu_B(g_L\,\boldsymbol{L} + g_S\,\boldsymbol{S})$, resulting in a number of levels with the splitting given by

$$\Delta E(LSM_LM_S) = -\mu_B B(M_L + 2\,M_S). \tag{378}$$

In normal magnetic fields (say smaller or of the order of 1 T), the splittings are only fractions of an eV and there are other effects causing different splitting patterns, such as the $\boldsymbol{L}\cdot\boldsymbol{S}$ spin-orbit interaction. But for very large magnetic fields one does see the above *normal Zeeman splitting* pattern.



Zeeman splitting of levels in a magnetic field (no spin-orbit). Also indicated are the transitions, separated into $\Delta M_L = 0$ (π-transitions) and $\Delta M_L = \pm 1$ (σ-transitions).

Finally we note that the magnetic effects discussed here are those in an external magnetic field. This defines a preferential direction in space and leads to dependence on eigenvalues of the (z-)component of the angular momentum operators. This is also found back in the names *magnetic* quantum numbers for m_ℓ, m_s, etc.

20.2 Spin-orbit interaction and magnetic fields

Inclusion of the spin-orbit interaction is important to describe the fine structure of the multiplets in atomic spectra. This fine structure in general turns out to be considerably larger than the magnetically induced splittings. In that case one cannot simply use the results for the normal Zeeman effect when spin plays a role. So consider the situation that one has an interaction term in the atom of the form

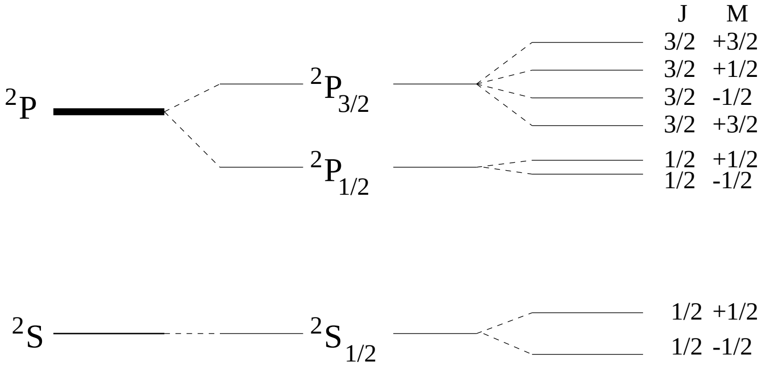
$$H_{\rm int} = A\,\boldsymbol{L}\cdot\boldsymbol{S} - \boldsymbol{\mu}\cdot\boldsymbol{B}, \tag{379}$$

with $\boldsymbol{\mu} = \mu_B(g_L\boldsymbol{L} + g_S\boldsymbol{S})/\hbar = \mu_B\,(\boldsymbol{L} + 2\,\boldsymbol{S})/\hbar$. We have already seen what happens in the situations $A = 0$ and $B = |\boldsymbol{B}| = 0$. One has

$$\begin{aligned} A = 0: \quad & \text{eigenstates} \quad |(\ldots)LSM_LM_S\rangle, \\ & \Delta E(LSM_LM_S) = \mu_B B(M_L + 2M_S), \end{aligned}$$

$$\begin{aligned} B = 0: \quad & \text{eigenstates} \quad |(\ldots)LSJM\rangle, \\ & \Delta E(LSJM) = \frac{1}{2}\,A\hbar^2\left[J(J+1) - L(L+1) - S(S+1)\right]. \end{aligned}$$

The splitting pattern for $A = 0$ has already been given, for $B = 0$ it splits the ${}^{2S+1}L$ multiplet into the different ${}^{2S+1}L_J$ multiplets, for the ${}^2P \rightarrow {}^2S$ transition indicated as the first splitting in the figure below.



The spin-orbit splitting leading to the ${}^{2S+1}L_J$ multiplets for the ${}^2P$ and ${}^2S$ levels and the consecutive splitting in a magnetic field for the case of a small magnetic field.

When one switches on the magnetic field, one deals with an interaction term for which neither $|LSM_LM_S\rangle$, nor $|LSJM\rangle$ are proper states (check compatibility of the relevant operators!). If the magnetic field is small the states will be in first order given by $|LSJM\rangle$ and one can calculate the energy shift via

$$\Delta E_{\text{mag}} = \mu_B B\, \langle(\ldots)LSJM|L_z + 2S_z|(\ldots)LSJM\rangle = \mu_B B\, \langle(\ldots)LSJM|J_z + S_z|(\ldots)LSJM\rangle. \tag{380}$$

The part with which we need to be careful is the expectation value of S_z, Evaluating it between states with different M-values belonging to the same J gives zero, because if two M values involve the same M_S, the M_L's must be different (remember that in the coupling $M = M_L + M_S$). Thus we just need

$$\langle LSJM|S_z|LSJM\rangle = M\,\frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{381}$$

which follows from a subtle relation involving $\boldsymbol{S}$ and $\boldsymbol{J}$ operators[7], $\boldsymbol{J}^2 S_z + S_z \boldsymbol{J}^2 = 2\,J_z\,(\boldsymbol{J}\cdot\boldsymbol{S})$ leading to

$$\Delta E_{\text{mag}} = \underbrace{\left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}\right]}_{g_J} M\,\mu_B B, \tag{382}$$

where g_J is called the Landé factor. This splitting is also indicated in the figure. Note that the procedure only works for small B-values. For large B-values (Paschen-Back limit) the assumption of states being approximately given by $|LSJM\rangle$ is not valid and one gets the previously discussed normal Zeeman splitting.

Exercises

Exercise 20.1

A particle is put in a magnetic field $\boldsymbol{B}$ with strength B_0. The field is parallel to the z-axis. The Hamiltonian is given by $H = -\gamma\,\boldsymbol{S}\cdot\boldsymbol{B}$. At time $t = 0$ the particle is in the spin state

$$\chi(0) = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}.$$

(a) Give the matrix representation of the Hamiltonian.

---

[7] From $[J_i, A_j] = i\hbar\epsilon_{ijk}A_k$ one obtains the relations $[\boldsymbol{J}^2, A_i] = -i\hbar\epsilon_{ikl}(J_kA_l + A_lJ_k)$, which yields $[\boldsymbol{J}^2, [\boldsymbol{J}^2, A_i]] = 2\hbar^2(\boldsymbol{J}^2A_i + A_i\boldsymbol{J}^2) - 4\hbar^2(\boldsymbol{A}\cdot\boldsymbol{J})J_i$.

(b) Calculate the state vector of the particle at time $t > 0$.

(c) Give the time dependence of the expectation value of S_x.

Exercise 20.2

(a) Use for the ${}^2P$ states the basis states $|L, S; M_L, M_S\rangle$ and write down the spin-orbit hamiltonian $H_{\text{so}} = A\,\boldsymbol{L} \cdot \boldsymbol{S}$ as a matrix. Use for this the explicit expression

$$H_{\text{so}} = \frac{A}{2}\,(2\,L_z S_z + L_+ S_- + L_- S_+)\,.$$

Determine the eigenvalues and eigenstates. The latter are of course precisely the $|L, S; J, M\rangle$ states.

(b) On the same basis, write down the hamiltonian in an external magnetic field, $H_{\text{int}} = A\,\boldsymbol{L} \cdot \boldsymbol{S} - \boldsymbol{\mu} \cdot \boldsymbol{B}$, using the explicit form

$$H_{\text{int}} = \frac{A}{2}\,(2\,L_z S_z + L_+ S_- + L_- S_+) - \mu_B\, B_0\,(L_z + 2\,S_z)\,.$$

Find all eigenvalues and check that they coincide with the approximations made for small and large B-fields.

21 Variational approach

21.1 Basic treatment

The variational method is used to obtain an estimate for the ground state energy and the ground state wave function for a given hamiltonian. This is done by taking a trial wave function $|\psi_{[\alpha_1,\alpha_2,\ldots]}\rangle$ depending on a number of parameters α_i and calculating the expectation value for the (given) hamiltonian,

$$E_{[\alpha_1,\alpha_2,\ldots]} = \frac{\langle\psi_{[\alpha_1,\alpha_2,\ldots]}|H|\psi_{[\alpha_1,\alpha_2,\ldots]}\rangle}{\langle\psi_{[\alpha_1,\alpha_2,\ldots]}|\psi_{[\alpha_1,\alpha_2,\ldots]}\rangle}. \tag{383}$$

It is a simple exercise to show that if the true solutions and energies of H are given by $(H - E_n)\,|\phi_n\rangle = 0$, that

$$E_{[\alpha_1,\alpha_2,\ldots]} \geq E_0, \tag{384}$$

with the equal sign being true if $|\psi_{[\alpha_1,\alpha_2,\ldots]}\rangle = \phi_0$. By minimizing the expectation value of the hamiltonian by varying the parameters,

$$\frac{\partial E_{[\alpha_1,\alpha_2,\ldots]}}{\partial\alpha_i} = 0, \tag{385}$$

one hopes to get close to the true ground state. The succes of the method not only depends on the number of parameters used and the calculational power of computers, but also on smart choices for the trial wave function such as choosing the correct symmetry, the correct number of nodes and the correct asymptotic (large and small r) behavior of the wave function.

If one wants to apply variational methods to find other (higher-lying) states, one must ensure that the trial function is chosen to be orthogonal to any lower state. This may be achieved by looking for states with a particular symmetry, which of course (why?) only works if the Hamiltonian one is working with, has this symmetry. In this way one can look for the lowest p-wave in radially symmetric Hamiltonian by using an ansatz of the form $\psi \propto z\,f(r)$. One might also constrain oneself to wave functions which always have a node, keeping in mind the node theorem for bound states.

21.2 Application: ground state of Helium atom

As a trial function for the He ground a good ansatz could be a simple product of wave functions,

$$\psi_T(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{\alpha^3}{\pi\,a_0^3}\,e^{-\alpha\,r_1/a_0}\,e^{-\alpha\,r_2/a_0}. \tag{386}$$

By allowing the coefficient α in the exponent to vary, we try to incorporate the screening. We can use the variational approach to see how well we can do. With the results from the sections on the hydrogen atom and those of the previous section we find

$$\langle\psi_T| -\frac{\hbar^2}{2m}\left(\boldsymbol{\nabla}_1^2 + \boldsymbol{\nabla}_2^2\right)|\psi_T\rangle = \frac{\hbar^2}{m\,a_0^2}\,\alpha^2 = 2\,\alpha^2\,R_\infty, \tag{387}$$

$$\langle\psi_T|\frac{-Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)|\psi_T\rangle = -\frac{2Ze^2}{4\pi\epsilon_0\,a_0}\,\alpha = -4\,Z\alpha\,R_\infty, \tag{388}$$

$$\langle\psi_T|\frac{e^2}{4\pi\epsilon_0\,r_{12}}|\psi_T\rangle = \frac{5}{4}\,\alpha\,R_\infty, \tag{389}$$

and thus

$$E_{[\alpha]} = 2\left[\alpha^2 - \left(2Z - \frac{5}{8}\right)\alpha\right]R_\infty, \tag{390}$$

which is minimized for

$$\alpha = Z_{\rm eff} = Z - \frac{5}{16} \tag{391}$$

with

$$E[\alpha_{\rm min}] = -2\left(Z - \frac{5}{16}\right)^2 R_\infty. \tag{392}$$

For He this gives $E_{\rm gs} = -5.7\,R_\infty$, wich is within a few percent of the experimental value of $-5.81\,R_\infty = 79.0$ eV and much better than the perturbative value discussed in section 19.3 (which of course is just the result obtained for $\alpha = 2$). As expected the value $Z_{\rm eff} = 27/16$ is less than 2.

21.3 Application: ionization energies and electron affinities

Some results that we have encountered in previous sections are

$$\begin{aligned} &\mathrm{H}^+ + e^- = \mathrm{H} + \ 13.6 \text{ eV}, \\ &\mathrm{He}^{++} + e^- = \mathrm{He}^+ + \ 54.4 \text{ eV}, \end{aligned}$$

Adding another electron in the latter case yields

$$\mathrm{He}^+ + e^- = \mathrm{He} + \ 24.6 \text{ eV}, \tag{393}$$

showing that adding electrons one gains less energy if there are already other electrons. The energy one gains in adding the last electron is the *ionization energy.* In many cases one can still add additional electrons and gain some energy, which is called the *electron affinity* E.g. for Chlorine

$$\begin{aligned} &\mathrm{Cl}^+ + e^- = \mathrm{Cl} + \ 13.0 \text{ eV}, \\ &\mathrm{Cl} + e^- = \mathrm{Cl}^- + \ 3.6 \text{ eV}. \end{aligned}$$

The binding energy of Chlorine is 13.0 eV, the electron affinity is 3.6 eV. Electron affinities play a role in molecular binding.

An interesting example is actually the hydrogen atom, which also has a positive electron affinity,

$$\mathrm{H} + e^- = \mathrm{H}^- + \ 0.76 \text{ eV}.$$

The H atom, however, also illustrates that adding a second electron completely changes the structure of the wave functions. Adding one electron to H^+ or He^{++} one has simple hydrogen-like wave functions. But adding the second electron one has to account for the presence of the other electron as illustrated for He using the variational approach. In that case a product wave function still worked fine. If one tries for a second electron in H^- such a product wave function one does not find a positive electron affinity. In order to find a positive electron affinity for the H-atom (for which an equivalent statement is that the H^--ion has a binding energy of $0.056\,R_\infty = 0.76$ eV) one can use e.g. a trial function of the form

$$\psi_T = C\left[e^{-(\alpha_1 r_1 + \alpha_2 r_2)/a_0} + e^{-(\alpha_1 r_2 + \alpha_2 r_1)/a_0}\right]. \tag{394}$$

The form is suggestive for two different orbits with fall-off parameters α_1 and α_2, but as electrons are indistinguishable one must (anti)-symmetrize (depending on spin) the two terms. With a plus sign one has wave functions without nodes giving the lowest energy.

Questions and exercises

1. What does one know about the relation between the energy found in the variational approach and the true ground state energy?
2. Same question for the wave function?
3. In looking for an approximation to the energy of the first excited state, the trial wave function must be orthogonal to the wave function of the ground state. Is it sufficient to ensure that the trial wave function is orthogonal to the 'best' ground state wave function found in the variational approach?
4. Why will the choice with a plus sign in the 'two-orbit' wave function in Eq. 394 give a lower energy than the minus choice?

Exercise 21.1

(a) Estimate the ground state energy in a linear potential, $V(r) = T_0\, r$. Some useful integrals might be

$$\int_0^\infty dr\; r^\alpha \,\exp(-Ar) = \frac{\Gamma(\alpha+1)}{A^{\alpha+1}},$$
$$\int_0^\infty dr\; r^{\frac{3}{2}\alpha} \,\exp\left(-Ar^{3/2}\right) = \frac{2}{3}\,\frac{\Gamma\left(\alpha+\frac{2}{3}\right)}{A^{\alpha+\frac{2}{3}}},$$
$$\int_0^\infty dr\; r^{2\alpha} \,\exp\left(-Ar^{2}\right) = \frac{1}{2}\,\frac{\Gamma\left(\alpha+\frac{1}{2}\right)}{A^{\alpha+\frac{1}{2}}},$$

valid for $\alpha \ge 0$. Note that $\Gamma(z+1) = z!$, satisfying $\Gamma(z+1) = z\Gamma(z)$. Some specific values are $\Gamma(1) = 0! = 1$, $\Gamma(1/2) = \sqrt{\pi}$, and $\Gamma(2/3) = 1.35412$.

(b) To appreciate the accuracy of your result, note that the exact solution is an Airy function $Ai(z)$, solution of $Ai''(z) - z\,Ai(z) = 0$. Argue that the function

$$u(r) \sim Ai\left(\frac{r}{r_0} - \epsilon\right).$$

with $r_0 = (\hbar^2/2mT_0)^{1/3}$ is a solution of the three-dimensional linear potential if $Ai(-\epsilon) = 0$. Show that it represents a solution with boundary condition $u(0) = 0$ and energy $E = -\epsilon\, E_0$ where $E_0 = (\hbar^2 T_0^2/2m)^{1/3}$. The first (negative) zero of the Airy function is at $\epsilon = 2.3381$.

Exercise 21.2

Apply the variational principle to find a suitable wave function for H$^-$. Try the product wave function in Eq. 394 that has been used for He. What do you find for the electron affinity of H in that case. Then try the two-orbit form proposed in this chapter and show that it at least leads to a positive electron affinity. A useful integral is

$$\int d^3r_1\, d^3r_2\; \frac{e^{-2\alpha_1 r_1 - 2\alpha_2 r_2}}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \left(\frac{\pi}{\alpha_1^3}\right)\left(\frac{\pi}{\alpha_2^3}\right)\frac{\alpha_1\alpha_2\,\left(\alpha_1^2+\alpha_2^2+3\,\alpha_1\alpha_2\right)}{(\alpha_1+\alpha_2)^3} \overset{\alpha_1=\alpha_2}{=} \frac{5}{8}\,\alpha\left(\frac{\pi}{\alpha^3}\right)^2 .$$

22 Time-dependent perturbation theory

22.1 Explicit time-dependence

For a hamiltonian without explicit time-dependence, i.e. $H = H(\boldsymbol{r}, \boldsymbol{p}, \ldots)$ one has stationary state solutions of the form $|\phi_n\rangle\, e^{-iE_n t/\hbar}$, where $|\phi_n\rangle$ are the time-independent solutions of the eigenvalue equation $H(\boldsymbol{r}, \boldsymbol{p}, \ldots)|\phi_n\rangle = E_n|\phi_n\rangle$. This can be checked by inserting $|\psi_n(t)\rangle = c_n(t)|\phi\rangle$ into the Schrödinger equation,

$$i\hbar \frac{\partial|\psi\rangle}{\partial t} = H|\psi(t)\rangle$$

leading to $i\hbar\frac{d}{dt}c_n(t) = E_n\, c_n(t)$. As discussed earlier, there are two possibilities

1. One starts (e.g. after a measurement) with $\psi(0) = |\phi_i\rangle$, where ϕ_i is one of the eigenstates of H with eigenvalue/energy E_i. In that case $|\psi(t)\rangle = |\phi_i\rangle\, e^{-iE_i t/\hbar}$ and all expectation values of operators (that do not explicitly depend on time) are time-independent.

2. One starts in a mixed state, say $|\psi(0)\rangle = |\phi_1\rangle + |\phi_2\rangle$. In that case one has $|\psi(t)\rangle = |\phi_1\rangle\, e^{-iE_1 t/\hbar} + |\phi_2\rangle\, e^{-iE_2 t/\hbar}$ or $|\psi(t)\rangle \propto |\phi_1\rangle + |\phi_2\rangle\, e^{-i(E_2-E_1)t/\hbar}$, which leads to oscillations in expectation values with frequency $\sim (E_2 - E_1)/\hbar$.

In the situation that the hamiltonian of a system contains explicit time dependence, i.e. $H = H(\boldsymbol{r}, \boldsymbol{p}, \ldots, t)$ one no longer has simple stationary state solutions of the form $|\phi\rangle\, e^{-iEt/\hbar}$.

We consider the case that the time-dependence is contained in a part of the Hamiltonian. Since we will also treat this part in perturbation theory we multiply with a factor λ to keep track of orders,

$$H = H_0 + \lambda\, V(t). \tag{395}$$

The part H_0 does not have explicit t-dependence, while the second part has a (possible) time-dependence. Assume the problem H_0 to be known with eigenstates $|\phi_n\rangle$ and eigen-energies $E_n^{(0)}$. When doing time-independent perturbation theory (which is of course also possible when V is time-independent) one tries to express the true eigenfunctions of H in the complete set ϕ_i. In the present treatment one makes the observation that if the system at some time is in a state $|\phi_i\rangle$, it will at a later time no longer be in this state. The calculation of the rate of change is what is done in time-dependent perturbation theory. As already mentioned this can be used for both time-independent and time-dependent perturbations.

As stated, we assume a known (time-independent) part H_0, for which the eigenstates and eigen-energies satisfy $H_0|\phi_n\rangle = E_n^{(0)}|\phi_n\rangle$. Using completeness of the states $|\phi_n\rangle$ we know that it is always possible to write

$$|\psi(t)\rangle = \sum_n c_n(t)\, |\phi_n\rangle\, e^{-iE_n^{(0)} t/\hbar}. \tag{396}$$

Note that one could have absorbed the exponential time-dependence in $c_n(t)$, but not doing so is more appropriate in perturbation theory. In the choosen way of proceeding, the time-dependence of c_n is solely a consequence of $\lambda\, V$.

By substituting the expression for $|\psi(t)\rangle$ in the Schrödinger equation,

$$i\hbar\, \frac{\partial}{\partial t}|\psi(t)\rangle = (H_0 + \lambda\, V(t))\, |\psi(t)\rangle, \tag{397}$$

one simply finds

$$i\hbar\, \dot{c}_p(t) = \sum_n \lambda\, V_{pn}(t)\, c_n(t)\, e^{+i\,\omega_{pn} t}, \tag{398}$$

where $V_{pn} = \langle\phi_p|V(t)|\phi_n\rangle$ is the expectation value of the potential $V(t)$ between the (time-independent) eigenstates of H_0, and $\omega_{pn} = (E_p^{(0)} - E_n^{(0)})/\hbar$. As promised if $\lambda\, V(t) = 0$, the righthand-side is zero and the coefficients are time-independent.

In the next section we solve the above equations for a simple two-state system. More often, however, one will encounter a perturbative approach.

In the case of perturbation theory, we realize that in trying a solution of the form

$$c_p(t) = c_p^{(0)}(t) + \lambda\, c_p^{(1)}(t) + \ldots, \tag{399}$$

the time-dependence of a specific order is determined by the next lower order,

$$i\hbar\, \dot{c}_p^{(m+1)} = \sum_n V_{pn}(t)\, c_n^{(m)}(t)\, e^{+i\,\omega_{pn}t}. \tag{400}$$

Starting with $c_p(0) = \delta_{pi}$ one immediately sees that the first two orders are given by

$$c_p^{(0)}(\tau) = \delta_{pi}, \tag{401}$$

$$c_p^{(1)}(\tau) = \frac{1}{i\hbar}\int_0^\tau dt\; V_{pi}(t)\, e^{+i\,\omega_{pi}t}. \tag{402}$$

This can straightforwardly been extended and leads to the socalled 'time-ordered' exponential, which we will not discuss here.

The quantity $|c_p(\tau)|^2$ is the probability to find the system in the state $|\phi_p\rangle$, which means the probability for a transition $i \rightarrow p$. The first order result is valid if $|c_p^{(0)}(\tau) + c_p^{(1)}(\tau)|^2 \approx 1$.

22.2 Application: magnetic resonance

Consider the following hamiltonian for a two-state system,

$$H = -\boldsymbol{\mu}\cdot\boldsymbol{B}(t) = -\gamma\,\boldsymbol{s}\cdot\boldsymbol{B}(t), \tag{403}$$

describing the interaction of a spinning particle (with magnetic moment μ proportional to its spin) in a magnetic field. For instance for an elementary electron $\boldsymbol{\mu} = -(e/m)\,\boldsymbol{s}$ where $\boldsymbol{s} = (\hbar/2)\,\boldsymbol{\sigma}$. For other (composite particles) the factor may be different. However, for any spin 1/2 particle the spin operators can be represented by the Pauli matrices.

Considering first the case of a constant magnetic field in (say) the z-direction, i.e. $\boldsymbol{B}_0 = (0, 0, B_0)$. Using the matrix representation for a spin 1/2 particle one has

$$H_0 = -\frac{\gamma B_0}{2}\,\hbar\,\sigma_z = -\frac{\gamma B_0}{2}\,\hbar\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{404}$$

The solutions are easily obtained,

$$|\phi_1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{with} \quad E_1^{(0)} = -\frac{\gamma B_0}{2}\,\hbar, \tag{405}$$

$$|\phi_2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{with} \quad E_2^{(0)} = \frac{\gamma B_0}{2}\,\hbar, \tag{406}$$

If the system is in a spin-state along the z-direction, it will stay in this state. If it is in another direction, it will start to oscillate with a frequency $\omega_{12} = (E_1^{(0)} - E_2^{(0)})/\hbar = -\gamma\, B_0$.

Next consider the system in a circulating magnetic field in the x-y plane, superimposed on $\boldsymbol{B}_0$, $\boldsymbol{B}(t) = \boldsymbol{B}_0 + \boldsymbol{B}_1(t)$, where $\boldsymbol{B}_1(t) = (B_1 \cos\omega t, B_1 \sin\omega t, 0)$. In that case

$$\begin{aligned} H &= -\frac{\gamma B_0}{2}\,\hbar\,\sigma_z - \frac{\gamma B_1}{2}\,\hbar(\sigma_x \cos\omega t + \sigma_y \sin\omega t) \\ &= -\frac{\gamma B_0}{2}\,\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \frac{\gamma B_1}{2}\,\hbar \begin{pmatrix} 0 & e^{-i\omega t} \\ e^{+i\omega t} & 0 \end{pmatrix}. \end{aligned} \tag{407}$$

As discussed in the previous section we can assume

$$|\psi(t)\rangle = c_1(t) \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-i\omega_{12}t/2} + c_2(t) \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{+i\omega_{12}t/2} = \begin{pmatrix} c_1(t)\, e^{-i\omega_{12}t/2} \\ c_2(t)\, e^{+i\omega_{12}t/2} \end{pmatrix}, \tag{408}$$

for which insertion in the Schrödinger equation or using the theory in the previous section gives

$$\begin{aligned} i\hbar \begin{pmatrix} \dot c_1(t) \\ \dot c_2(t) \end{pmatrix} &= -\frac{\gamma B_1}{2}\,\hbar \begin{pmatrix} 0 & e^{-i(\omega-\omega_{12})t} \\ e^{+i(\omega-\omega_{12})t} & 0 \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} \\ &= \hbar \begin{pmatrix} 0 & v(t) \\ v^*(t) & 0 \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}, \end{aligned} \tag{409}$$

with $|v| = \gamma B_1/2$. The coupled equations,

$$i\,\dot c_1(t) = v(t)\, c_2(t), \tag{410}$$

$$i\,\dot c_2(t) = v^*(t)\, c_1(t), \tag{411}$$

can be simply rewritten into a second order differential equation for c_1,

$$\ddot c_1 + i(\omega - \omega_{12})\,\dot c_1 + |v|^2\, c_1 = 0. \tag{412}$$

This equation has two independent solutions of the form $e^{i\,pt}$ with

$$p = -\frac{1}{2}\,(\omega - \omega_{12}) \pm \frac{1}{2}\,\Delta \tag{413}$$

with $\Delta = \sqrt{(\omega-\omega_{12})^2 + 4|v|^2}$. The general solution can then be written as

$$\begin{aligned} c_1(t) &= e^{-\frac{1}{2}i(\omega-\omega_{12})t} \left(A \sin\frac{\Delta\,t}{2} + B \cos\frac{\Delta\,t}{2}\right), \\ c_2(t) &= \frac{i}{v(t)}\,\dot c_1(t). \end{aligned} \tag{414}$$

Starting off with $c_1(0) = 0$ and $|c_2(0)| = 1$, it is straightforward to check that

$$c_1(t) = A\, e^{\frac{1}{2}\,i\,(\omega-\omega_{12})t} \sin\frac{\Delta\,t}{2}, \tag{415}$$

$$|A|^2 = 4\,\frac{|v|^2}{\Delta^2} = \frac{\gamma^2 B_1^2}{(\omega-\omega_{12})^2 + \gamma^2 B_1^2}, \tag{416}$$

$$|c_1(t)|^2 + |c_2(t)|^2 = 1. \tag{417}$$

Thus, given an initial spin aligned parallel or antiparallel to the $\boldsymbol{B}_0$ field, the probability for transition to the other spin state shows oscillations with a frequency Δ, while the magnitude depends on the frequency of the rotating perpendicular $\boldsymbol{B}_1$ field, showing a resonance at $\omega = \omega_{12}$. In that case the spin completely flips from parallel to antiparallel and back with frequency Δ (at resonance we have $\Delta = \gamma B_1$). For further discussion and plots, see Mandl (section 9.2).

22.3 Fermi's golden rule

We now return to the perturbative treatment of time-dependence and note that also for a time-independent interaction V, transitions occur, if the initial state is not an eigenstate of the full Hamiltonian, but only of H_0. If V is sufficiently weak, we find the result in first order perturbation theory,

$$\begin{aligned} c_p^{(1)}(\tau) &= \frac{V_{pi}}{i\hbar}\int_0^\tau dt\; e^{+i\,\omega_{pi}t} = -\frac{V_{pi}}{\hbar\omega_{pi}}\,e^{+i\,\omega_{pi}t}\Big|_0^\tau \\ &= \frac{V_{pi}}{\hbar\omega_{pi}}\left(1-e^{+i\,\omega_{pi}\tau}\right) = -\frac{2\,V_{pi}}{\hbar\omega_{pi}}\,\sin(\omega_{pi}\tau/2)\,e^{+i\,\omega_{pi}\tau/2}, \end{aligned} \tag{418}$$

and thus for $p \neq i$,

$$P^{(1)}_{i\to p}(\tau) = \frac{4\,|V_{pi}|^2}{\hbar^2}\,\frac{\sin^2(\omega_{pi}\tau/2)}{\omega_{pi}^2}. \tag{419}$$

The function

$$f(\omega_{pi}) = \frac{\sin^2(\omega_{pi}\tau/2)}{\omega_{pi}^2}$$

is for increasing times τ ever more strongly peaked around $\omega_{pi} = 0$. The value at zero is $f(0) = \tau^2/4$, the first zeros are at $|\omega_{pi}| = 2\pi/\tau$. Since

$$\int d\omega_{pi}\;\frac{\sin^2(\omega_{pi}\tau/2)}{\omega_{pi}^2} = \frac{\pi\,\tau}{2}, \tag{420}$$

we approximate

$$\frac{\sin^2(\omega_{pi}\tau/2)}{\omega_{pi}^2} = \frac{\pi\,\tau}{2}\,\delta(\omega_{pi}). \tag{421}$$

Then we find[8]

$$P^{(1)}_{i\to p}(\tau) = \tau\,\frac{2\pi}{\hbar}\,|V_{pi}|^2\,\delta(E_p - E_i) \tag{422}$$

or for the transition probability per unit time,

$$\dot P^{(1)}_{i\to p} = \frac{2\pi}{\hbar}\,|V_{pi}|^2\,\delta(E_p - E_i) \qquad \text{Fermi's Golden Rule.} \tag{423}$$

Although the allowed final state is selected via the energy delta function, it is often possible that the system can go to many final states, because we are dealing with a continuum. In that case one needs the *density of states* $\rho(E)$, where $\rho(E)\,dE$ is the number of states in an energy interval dE around E. The transition probability per unit time is then given by

$$\dot P^{(1)}_{i\to p} = \int dE_f\,\rho(E_f)\,\frac{2\pi}{\hbar}\,|V_{fi}|^2\,\delta(E_f - E_i) = \frac{2\pi}{\hbar}\,|V_{pi}|^2\,\rho(E_p)\Big|_{E_p=E_i} \tag{424}$$

(Fermi's Golden Rule No. 2).

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[8] $\delta(ax) = \frac{1}{|a|}\,\delta(x)$

22.4 Application: emission and absorption of radiation by atoms

As an example of time-dependent perturbations, we discuss the absorption and emission of photons by atoms. In the dipole approximation one finds as the dominant term in a partial wave expansion of the radiation field corresponding to a photon field with polarization $\boldsymbol{\epsilon}$ (fields derived from vector potential $\boldsymbol{A} = \boldsymbol{\epsilon}\,(c\,E_0/i\,\omega)\,\exp[i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)]$ using $c\boldsymbol{E} = -\partial\boldsymbol{A}/\partial t)$ and $\boldsymbol{B} = \boldsymbol{\nabla}\times\boldsymbol{A}$) the following (time-dependent) interaction

$$V(t) = -\boldsymbol{D}\cdot\boldsymbol{E}(t) = -\boldsymbol{D}\cdot\boldsymbol{\epsilon}\,E_0\,e^{-i\,\omega t}, \tag{425}$$

where

$$\boldsymbol{D} = \int d^3r\;\boldsymbol{r}\,\rho(\boldsymbol{r}) \Longrightarrow \sum_i q_i\,\boldsymbol{r}_i. \tag{426}$$

The results after the arrow in the above equation indicate the results for a number of charges q_i at position $\boldsymbol{r}_i$, i.e. $\rho(\boldsymbol{r}) = \sum_i q_i\,\delta^3(\boldsymbol{r}-\boldsymbol{r}_i)$. For a neutral system the first interaction term disappears and the next important one is the interaction with the electric dipole moment ($\boldsymbol{D}$).

Although we have a time-dependent interaction, we can proceed as in the derivation of Fermi's golden rule. We obtain now

$$c_p^{(1)}(\tau) = \frac{\langle\phi_p|\boldsymbol{D}\cdot\boldsymbol{\epsilon}|\phi_i\rangle\,E_0}{i\hbar}\;\frac{e^{i\,(\omega_{pi}-\omega)\tau}-1}{i\,(\omega_{pi}-\omega)}, \tag{427}$$

which gives as before rise to a delta function $\delta(\omega-\omega_{pi})$. With ω being the positive photon frequency, this can only describe *absorption* of a photon, $\hbar\omega = E_p - E_i > 0$. For the real electromagnetic fields also the complex conjugate solution must be considered, which gives the same result with $\omega \to -\omega$. This gives rise to a delta function $\delta(\omega+\omega_{pi})$ and describes the *emission* of a photon, $\hbar\omega = -\hbar\omega_{pi} = E_i - E_p > 0$. The transition probability can be summarized by

$$P_{i\to p}^{(1)}(\tau) = \frac{E_0^2(\omega)}{\hbar^2}\,|\langle\phi_p|\boldsymbol{D}\cdot\boldsymbol{\epsilon}|\phi_i\rangle|^2\,\frac{\pi\,\tau}{2}\,\delta(\omega-|\omega_{pi}|). \tag{428}$$

If one is not working with monochromatic light one has an integral over different frequencies ω. Instead of the intensity of the field $E_0 = E_0(\omega)$ one can use the number of incident photons $N(\omega)$ (number/(area×time)). This number is determined by equating the energy densities in a frequency interval $d\omega$,

$$\frac{1}{2}\,\epsilon_0\,E_0^2(\omega)\,d\omega = \frac{N(\omega)\,\hbar\omega}{c}\,d\omega. \tag{429}$$

Integrating over the photon frequencies, one sees that the atom absorps or emits photons of the right frequency leading to a transition rate

$$\dot{P}_{i\to p}^{(1)} = \frac{\pi}{\epsilon_0\,\hbar c}\,|\omega_{pi}|\,N(|\omega_{pi}|)\,|\langle\phi_p|\boldsymbol{D}\cdot\boldsymbol{\epsilon}|\phi_i\rangle|^2. \tag{430}$$

For electrons $\boldsymbol{D} = -\sum_i e\,\boldsymbol{r}_i = -e\,\boldsymbol{R}$. For unpolarized light $\boldsymbol{\epsilon}$ is arbitrary and averaging gives a factor 1/3. In terms of the fine structure constant $\alpha = e^2/4\pi\,\epsilon_0\,\hbar c$ the averaged transition rate is

$$W_{i\to p} = \overline{\dot{P}_{i\to p}^{(1)}} = \frac{4}{3}\,\pi^2\,\alpha\,|\omega_{pi}|\,N(|\omega_{pi}|)\,|\langle\phi_p|\boldsymbol{R}|\phi_i\rangle|^2. \tag{431}$$

Note that by treating also the electromagnetic field quantummechanically one finds in addition to the *stimulated absorption or emission* rate a *spontaneous emission* rate

$$W_{i\to p}^{\text{spont.}} = \frac{4}{3}\,\alpha\,\frac{\omega_{ip}^3}{c^2}\,|\langle\phi_p|\boldsymbol{R}|\phi_i\rangle|^2, \tag{432}$$

governed by the same transition matrix element and thus obeying the same selection rules.

22.5 Application: unstable states

In many circumstances one encounters unstable states, i.e. the probability P to find a system in a particular state decreases in time,

$$P(t+dt) = P(t)\,(1-\gamma\,dt) \quad\Longrightarrow\quad \frac{dP}{dt} = -\gamma\,P(t),$$

where γ is the *decay rate* or decay probability per unit time. The solution is

$$P(t) = P(0)\,e^{-\gamma\,t} = P(0)\,e^{-t/T}, \tag{433}$$

with $T = 1/\gamma \equiv \hbar/\Gamma$ the *lifetime*. The quantity Γ is referred to as the *width* of a state. For a decaying state we thus write

$$|\psi_n(t)\rangle \propto e^{-i\,E_n t/\hbar - \gamma_n t/2}. \tag{434}$$

We can expand a decaying state in eigenmodes according to

$$e^{-i\,E_n t/\hbar-\gamma_n t/2}\,\theta(t) = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,c(\omega)\,e^{-i\,\omega t}, \tag{435}$$

with

$$\begin{aligned} c(\omega) &= \int_0^\infty dt\; e^{+i\,(\omega-\omega_n+i\gamma_n/2)t} \\ &= \frac{-i}{\omega-\omega_n+i\gamma_n/2} e^{+i\,(\omega-\omega_n+i\gamma_n/2)t}\Big|_0^\infty \\ &= \frac{i}{\omega-\omega_n+i\gamma_n/2}. \end{aligned} \tag{436}$$

For unstable states the transition amplitude for emission or absorption of a photon is then proportional to

$$\begin{aligned} T(\omega) &= \int \frac{d\omega_1'}{2\pi}\,\frac{d\omega_2'}{2\pi}\,c_2^*(\omega_2')\,c_1(\omega_1')\,2\pi\,\delta(\omega-\omega_1'+\omega_2') \\ &= \int \frac{d\omega'}{2\pi} c_2^*(\omega')\,c_1(\omega'+\omega) \\ &= \int \frac{d\omega'}{2\pi}\int_0^\infty dt_1 \int_0^\infty dt_2\; e^{-i\,(\omega'-\omega_2-i\gamma_2/2)t_2}\; e^{+i\,(\omega'+\omega-\omega_1+i\gamma_1/2)t_1} \\ &= \int_0^\infty dt_1 \int_0^\infty dt_2\; e^{+i\,(\omega_2+i\gamma_2/2)t_2}\; e^{+i\,(\omega-\omega_1+i\gamma_1/2)t_1}\;\delta(t_1-t_2) \\ &= \int_0^\infty dt\; e^{+i\,(\omega-\omega_{12}+i\gamma_{12}/2)t} = \frac{i}{\omega-\omega_{12}+i\gamma_{12}/2}, \end{aligned} \tag{437}$$

where $\omega_{12} = \omega_1 - \omega_2$ and $\gamma_{12} = \gamma_1 + \gamma_2$. Thus the line-intensity becomes instead of a delta-function $\delta(\omega - |\omega_{pi}|)$ proportional to

$$I(\omega) \propto |T(\omega)|^2 \propto \frac{1}{(\omega-\omega_{12})^2 + \gamma_{12}^2/4},$$

or normalizing to the peak intensity

$$I(\omega) = I_0\,\frac{\Gamma_{12}^2/4}{\hbar^2\,(\omega-\omega_{12})^2 + \Gamma_{12}^2/4}, \tag{438}$$

showing the reason for the name width. The quantity Γ_{12} is precisely the width of the peak at half-maximum intensity, when plotting I as a function of the photon energy $\hbar\omega$. The function is known as a Lorentzian distribution or a Breit-Wigner distribution.

Exercises

Exercise 22.1

In this exercise we consider the phenomenon of neutrino oscillations. In the decay of pions produced by cosmic rays two types of neutrinos are produced. They are produced together with a muon or an electron and correspondingly named muon-neutrino and electron-neutrino.

These types, however, appear to be different from 'free' neutrinos. In order to explain some recent experiments, one makes the assumption that a muon-neutrino produced in the atmosphere is a linear superposition of the two mass eigenstates ϕ_1 and ϕ_2. Taking these as basisstates, we then have at time $t = 0$,

$$\psi(0) = \phi_{\nu_\mu} \equiv \left(\begin{array}{c} \cos\theta \\ \sin\theta \end{array} \right).$$

(a) Denoting the energies of the free neutrino states with $E_1 = \hbar\omega_1$ and $E_2 = \hbar\omega_2$, give the probability for finding a muon neutrino at time t.

(b) Approximate the energies for free neutrinos with momentum p with different masses in the limit that the momentum $p \gg m_1 c$ and $p \gg m_2 c$. Calculate the energy difference $E_1 - E_2$.

(c) Give the probability of finding muon neutrinos as a function of distance travelled (L), their energy (E) and the mass difference (Δm^2) and determine the oscillation wavelength.

(d) Given an oscillation wavelength of the order of 1000 km for neutrinos with an energy of 1 GeV = 10^9 eV (note that $\hbar c = 0.2 \times 10^{-6}$ GeV m), calculate the mass/energy difference $\Delta m^2 c^4$ between the two neutrino mass eigenstates for that case.

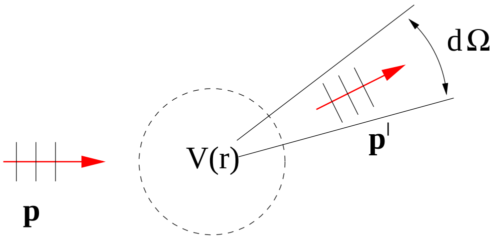
Exercise 22.2

In a system described by a one-dimensional harmonic oscillator (mass m and oscillator parameter ω) we apply a tiny squeezing force $F = -m\omega_1^2\, x$ (with $\omega_1 \ll \omega$) acting for a time-interval τ. Assuming that the system is in its groundstate at $t = 0$, in which state(s) will the system be found at time τ and what is the probability. Does it matter how long we apply the squeezing force?

23 Scattering theory

23.1 Differential cross sections

The quantummechanical treatment of a scattering problem is that of a particle (with mass m and incoming momentum $\boldsymbol{p}$) scattering in a given potential $V(\boldsymbol{r})$. We assume that the particle is scattered into a final state with momentum $\boldsymbol{p}'$. The latter is the result of a measurement with a detector with opening angle $d\Omega$, located under an angle $(\theta,\,\phi)$ with respect to the incoming momentum.



The number of scattered particles per unit time per solid angle, $n(\theta,\phi)$, is proportional to the incoming flux j_{in}, the number of particles per area per unit time,

$$n(\theta,\phi)\,d\Omega = |\boldsymbol{j}_{in}|\,d\sigma(\theta,\phi). \tag{439}$$

This is the definition of the *differential cross section* $d\sigma$, from which it should be immediately clear that the unit of cross section indeed is that of an area.

> *Typically cross sections have something to do with the area of the target as seen by the incoming particle, e.g. for proton-proton scattering a characteristic cross section is 40 mb, where 1 barn = 1 b* $\equiv 10^{-28}$ *m*^{2}*. The number 40 mb, indeed, is roughly equal to the area of a proton (with a radius of about 1 fm =* 10^{-15} *m). Besides the area of the target the cross sections also depends on the strength of the interaction. For instance electromagnetic interactions are typically a factor 100 or (100)*^{2} *smaller, e.g.* $\sigma_{\gamma p} \approx 100\ \mu b$ *and* $\sigma_{ep} \approx 1\mu b$*, corresponding to the presence of the fine structure constant* α *or* α^2 *respectively, where* $\alpha = e^2/4\pi\epsilon_0\hbar c$ *= 1/137. Weak interactions, e.g. neutrino-proton scattering, again have much smaller cross section in the order of* 10^{-2} *pb, indicative for the weakness of the "weak" interactions.*

23.2 Cross section in Born approximation

We use the result of time-dependent perturbation theory to obtain an expression for the cross section, namely the unperturbed situation is the free case, with as possible solutions, the incoming particle in a plane wave, $\phi_i(\boldsymbol{r}) = \sqrt{\rho}\,\exp\left(i\,\boldsymbol{p}\cdot\boldsymbol{r}/\hbar\right)$, with energy $E = \boldsymbol{p}^2/2m$ and the detected final state, $\phi_f(\boldsymbol{r}) = \sqrt{\rho}\,\exp\left(i\,\boldsymbol{p}'\cdot\boldsymbol{r}/\hbar\right)$, with energy $E' = \boldsymbol{p}'^2/2m$. Note that we allow processes in which the energy of the scattered particle changes. writing $Q \equiv E' - E$ one has $Q = 0$ for an elastic scattering process, an energy release, $Q > 0$, for an exothermic process and energy absorption, $Q < 0$, for an endothermic process. The potential V is a perturbation that can cause transitions between these states. Using Fermi's golden rule, we have for the number of particles with momentum $\boldsymbol{p}'$ (of which the direction with respect to $\boldsymbol{p}$ is given by the angles θ,ϕ),

$$n(\theta,\phi)\,d\Omega = \frac{2\pi}{\hbar}\left[|\langle\phi_f|V|\phi_i\rangle|^2\;\rho(E')\right]_{E'=E+Q}. \tag{440}$$

In order to get $d\sigma$ we need to get the flux $\mathscr{J}$ in the initial state and the density of states $\rho(E')$ in the final state.

- *Initial state flux.*
  The initial state flux is obtained from the wave function in the initial state via the expression for the current,
  $$\boldsymbol{j}(\boldsymbol{r},t) = \frac{\hbar}{2i\,m}\,(\psi^*\,\boldsymbol{\nabla}\psi - (\boldsymbol{\nabla}\psi)^*\psi) = \rho\,\frac{\boldsymbol{p}}{m} = \rho\,\boldsymbol{v}. \tag{441}$$
  The incoming flux is along $\boldsymbol{p}$ and, as expected, given by $\mathscr{I} = \rho\,v = \rho\,p/m$ (we use $p = |\boldsymbol{p}|$).
- *Final state density of states.* The final states are plane waves and the density of plane waves is in momentum space given by
  $$\rho(\boldsymbol{p})\,d^3p = \frac{1}{\rho}\,\frac{d^3p}{(2\pi\hbar)^3}. \tag{442}$$
  This can be seen by looking at the expansion of the unit operators in coordinate and momentum space consistent with the choice of the normalization of the plane waves,
  $$\mathbf{1} = \int d^3r\ |\boldsymbol{r}\rangle\,\langle\boldsymbol{r}| = \frac{1}{\rho}\int\frac{d^3p}{(2\pi\hbar)^3}\ |\boldsymbol{p}\rangle\,\langle\boldsymbol{p}|. \tag{443}$$
  Another way is to use box normalization, in which case one finds that for one particle in a box with sides L, i.e. $0 \le x \le L$, $0 \le y \le L$ and $0 \le z \le L$ (i.e. density $\rho = 1/L^3$), the wave function is found after imposing periodic boundary conditions,
  $$\phi_p(\boldsymbol{r}) = \frac{1}{L^{3/2}}\,\exp(i\,\boldsymbol{p}\cdot\boldsymbol{r}/\hbar), \tag{444}$$
  with $\boldsymbol{p} = (2\pi\hbar/L)\,(n_x, n_y, n_z)$, showing a density of states in p-space given by $(L/2\pi\hbar)^3$. Rewriting the final state density $\rho(\boldsymbol{p}')$ in terms of E' and Ω' we find
  $$\rho(\boldsymbol{p}')d^3p' = \frac{1}{\rho}\,\frac{p'^2}{(2\pi\hbar)^3}\,dp'\,d\Omega' = \frac{1}{\rho}\,\frac{m\,p'}{(2\pi\hbar)^3}\,dE'\,d\Omega' = \rho(E')\,dE'\,d\Omega'. \tag{445}$$

With the flux and density of final states, we get immediately

$$d\sigma(\theta,\phi) = d\Omega'\left(\frac{m}{2\pi\hbar^2}\right)^2\frac{p'}{p}\left|\int d^3r\ \exp\left(\frac{i}{\hbar}\,(\boldsymbol{p}-\boldsymbol{p}')\cdot\boldsymbol{r}\right)\ V(\boldsymbol{r})\right|^2_{E'=E+Q}, \tag{446}$$

or introducing the Fourier transform

$$\tilde{V}(\boldsymbol{k}) = \int d^3r\ V(\boldsymbol{r})\ \exp(i\,\boldsymbol{k}\cdot r), \tag{447}$$

one obtains the following expression for the differential cross section in the socalled *Born approximation*,

$$\frac{d\sigma}{d\Omega'} = \left(\frac{m}{2\pi\hbar^2}\right)^2\frac{p'}{p}\left|\tilde{V}(\boldsymbol{q})\right|^2, \tag{448}$$

where $\boldsymbol{q} = (\boldsymbol{p}-\boldsymbol{p}')/\hbar$ is the momentum transfer in the process. Often the differential cross section is azimuthally symmetric and one uses $d\Omega = d\cos\theta\,d\phi = 2\pi\,d\cos\theta$ to obtain $d\sigma/d\theta$. Integrating the differential cross section over all angles one obtains the *total cross section*,

$$\sigma(E) = \int d\Omega\ \frac{d\sigma}{d\Omega}(E,\Omega). \tag{449}$$

Note that in the case of elastic scattering one has $p' = p$ in which case the momentum transfer squared is given by

$$\begin{aligned} \hbar^2 \boldsymbol{q}^2 &= |\boldsymbol{p} - \boldsymbol{p}'|^2 = p^2 + p'^2 + 2\,pp'\,\cos(\theta) \\ &= 2\,p^2(1-\cos\theta) = 4\,p^2\,\sin^2(\theta/2). \end{aligned} \tag{450}$$

A dependence of the differential cross section $(d\sigma/d\Omega)(E,\theta)$ on this combination is a test for the validity of the Born approximation. This dependence is in particular applicable for central potentials, $V(\boldsymbol{r}) = V(r)$, in which case the Fourier transform

$$\begin{aligned} \tilde{V}(\boldsymbol{q}) &= \int d^3r\; V(r)\,\exp(i\,\boldsymbol{q}\cdot\boldsymbol{r}) \\ &= 2\pi \int_0^\infty dr \int_{-1}^1 d\cos\alpha\; r^2 V(r)\, e^{i\,qr\,\cos\alpha} \\ &= \frac{4\pi}{q}\int_0^\infty dr\; rV(r)\,\sin(qr), \end{aligned} \tag{451}$$

only depends on $q = |\boldsymbol{q}|$.

23.3 Applications to various potentials

The square well potential

As a first application consider the square well potential, $V(r) = V_0$ for $r \le a$ and zero elsewhere for sufficiently weak potentials at low energies and small angles ($qa \ll 1$). We will come back to the applicability of the Born approximation in a later section. The Fourier transform is given by

$$\begin{aligned} \tilde{V}(\boldsymbol{q}) &= \frac{4\pi\,V_0}{q}\int_0^a dr\; r\,\sin(qr) \\ &= \frac{4\pi\,V_0}{q^3}\int_0^{qa} dx\; x\,\sin(x) \\ &= \frac{4\pi\,V_0}{q^3}\left[\sin qa - qa\,\cos qa\right] \\ &\xrightarrow{qa\ll 1} \frac{4\pi\,V_0}{q^3}\left[qa - \frac{1}{3!}(qa)^3 - qa + \frac{1}{2!}(qa)^3 + \ldots\right] = \frac{4\pi}{3}\,V_0 a^3, \end{aligned} \tag{452}$$

leading for $E \to 0$ to

$$\frac{d\sigma}{d\Omega} \approx \frac{1}{9}\left(\frac{2m\,V_0\,a^2}{\hbar^2}\right)^2 a^2 \tag{453}$$

The Coulomb potential

The integral

$$\tilde{V}(\boldsymbol{q}) = -\frac{Ze^2}{4\pi\epsilon_0}\,\frac{4\pi}{q}\int_0^\infty dr\;\sin(qr) \tag{454}$$

diverges and we need to consider for instance the screened Coulomb potential, multiplied with $\exp(-\mu r)$. In that case one obtains

$$\begin{aligned}\tilde{V}(\boldsymbol{q}) &= -\frac{Ze^2}{4\pi\epsilon_0}\,\frac{4\pi}{q}\int_0^\infty dr\ \sin(qr)\,e^{-\mu r} \\ &= -\frac{Ze^2}{4\pi\epsilon_0}\,\frac{4\pi}{q}\int_0^\infty dr\ \frac{1}{2i}\left(e^{i(q+i\mu)r}-e^{i(q-i\mu)r}\right) \\ &= -\frac{Ze^2}{\epsilon_0}\,\frac{1}{q^2+\mu^2},\end{aligned} \tag{455}$$

allowing even the limit $\mu \to 0$ to be taken. Thus

$$\frac{d\sigma}{d\Omega}(E,\theta) = \left(\frac{m}{2\pi\,\hbar^2}\right)^2\left(\frac{Ze^2}{\epsilon_0}\right)^2\frac{1}{q^4} = \left(\frac{Ze^2}{8\pi\,\epsilon_0\,pv}\right)^2\frac{1}{\sin^4(\theta/2)}. \tag{456}$$

This result is known as the Rutherford cross section.

Processes near threshold

If the volume integral over the potential exists, one knows that $\tilde{V}(0)$ is finite and one sees that for small values of the momentum transfer one can write

$$\sigma(E) \ \propto\ \frac{p'}{p} \ =\ \sqrt{\frac{E'}{E}}. \tag{457}$$

Thus for an endothermic process (energy absorption or $Q < 0$) one has a threshold value for the incoming energy, $E_{\rm thr} = |Q|$ and one has for $E \approx E_{\rm thr}$

$$\sigma(E) \ \propto\ \sqrt{E - E_{\rm thr}}. \tag{458}$$

For an exothermic process (with energy release $Q > 0$) one can scatter for any (positive) energy E and one has near $E \approx 0$

$$\sigma(E) \ \propto\ \frac{1}{\sqrt{E}}. \tag{459}$$

Application to two-particle collisions

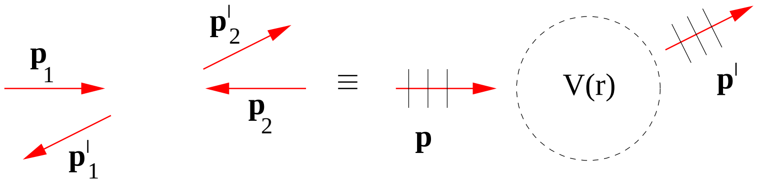
In most applications, the target is not an "external" potential, but rather two particles that collide (*collider experiments*) or one particle that is shot onto another one (*fixed target experiments*). This can in general lead to several possibilities corresponding to several *scattering channels*,

$$\begin{array}{lcll} a+b & \longrightarrow & a+b & \text{(elastic scattering)} \\ & \longrightarrow & c_1+c_2 & \multirow{2}{*}{\Big\}\ \text{(inelastic scattering)}} \\ & \longrightarrow & d_1+d_2+d_3 & \end{array} \tag{460}$$

Nevertheless, one can deal with these processes, at least the two → two ones, by considering the problem in the center of mass (CM) system. Considering two particles with momenta $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ and masses m_1 and m_2, for which the only translationally invariant interaction that is allowed must be of the form $V(\boldsymbol{r}_1 - \boldsymbol{r}_2) = V(\boldsymbol{r})$ with $\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2$ the relative coordinate. Since the flux factor is just given by

$$\mathscr{I} = \rho\,|\boldsymbol{v}_1 - \boldsymbol{v}_2| = \rho\left|\frac{\boldsymbol{p}_1}{m_1} - \frac{\boldsymbol{p}_2}{m_2}\right| = \rho\,\left|\frac{\boldsymbol{p}}{\mu}\right|, \tag{461}$$

where $\boldsymbol{p}$ is the relative momentum and μ the reduced mass one sees that the collision of *two* particles indeed can be described by considering the scattering of *one* particle with reduced mass μ having the relative momentum $\boldsymbol{p}$, scattering of the potential $V(\boldsymbol{r})$.



Notes:

- Note that in the scattering of *one* particle in an "external" potential, there is no translation invariance, hence no momentum conservation, while for *two* particles with a potential depending on the relative coordinate there is translation invariance. The latter requires conservation of the total momentum $\boldsymbol{P} = \boldsymbol{p}_1 + \boldsymbol{p}_2$, but not of the relative momentum.
- In the limit that one of the masses becomes very large, the light particle's momentum and mass, indeed, coincide with relative momentum and reduced mass, so one finds (consistently) that the heavy particle can be considered as scattering center.

Exercises

Exercise 23.1

Calculate the differential, $d\sigma/d\Omega(E,\theta)$, and total cross section, $\sigma(E)$ for $E = \hbar^2\,k^2/2m$ for a Yukawa potential

$$V(r) = V_0\,\frac{e^{-\mu\,r}}{r}.$$

Exercise 23.2

(a) Derive for elastic scattering the relativistic expression for $d\sigma/d\Omega(E,\theta)$. The differences with the nonrelativistic case are the use of a relativistic density ($\rho = E/mc^2$) and the use of the relativistic expression for the energy ($E = \sqrt{m^2c^4 + p^2c^2}$) and the velocity ($v = pc^2/E$) which will modify the form of the density of states $\rho(E)$.

(b) Derive the relativistic expression for the elastic Coulomb scattering cross section (note that Eq. 450 remains valid in the case of elastic scattering).

24 Scattering off a composite system

24.1 Form factors

Consider the scattering of an electron off an extended object, e.g. an atomic nucleus consisting of Z protons with charge $+e$ each (and N neutral neutrons) or an atom with a nucleus with charge $+Ze$ and Z electrons with charge $-e$ each. The hamiltonian is given by

$$H = H_{\rm system} + H_{\rm e} + V, \tag{462}$$

where $H_{\rm system}$ is the hamiltonian for the nucleus or the atom, $H_{\rm e}$ is the free electron hamiltonian and V describes the interaction between the scattering electron and the system. Let us start with the simplest situation in which the system is described by a wave function $\Psi(\boldsymbol{r}')$, remaining the same during the collision. The wave functions of the scattering electron in initial and final states are as before plane waves characterized by the momenta $\boldsymbol{p} = \hbar\boldsymbol{k}$ and $\boldsymbol{p}' = \hbar\boldsymbol{k}'$, respectively. The full initial state and final state wave functions are then $\Psi_i(\boldsymbol{r}) = \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r})\,\Phi(\boldsymbol{r}')$ and $\Psi_f(\boldsymbol{r}) = \exp(i\,\boldsymbol{k}'\cdot\boldsymbol{r})\,\Phi(\boldsymbol{r}')$, respectively. The Fourier transform of the potential needed in the cross section now becomes

$$\begin{aligned} V(\boldsymbol{q}) &= \int d^3r \int d^3r' \;\exp(-i\,\boldsymbol{k}'\cdot\boldsymbol{r})\,\Phi_B^*(\boldsymbol{r}')\frac{-e^2}{4\pi\,\epsilon_0\,|\boldsymbol{r}-\boldsymbol{r}'|}\,\Phi_A(\boldsymbol{r}')\,exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) \\ &= -\frac{e^2}{4\pi\,\epsilon_0}\int d^3r\;\exp(i\,\boldsymbol{q}\cdot\boldsymbol{r})\int d^3r'\,\frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}, \end{aligned} \tag{463}$$

which shows how the potential is modified by the fact that the system has a finite extension. To evaluate this, we exchange the integrations and introduce $\boldsymbol{r}'' = \boldsymbol{r} - \boldsymbol{r}'$ as integration variable to obtain

$$\begin{aligned} V(\boldsymbol{q}) &= -\frac{e^2}{4\pi\,\epsilon_0}\int d^3r'\;\exp(i\,\boldsymbol{q}\cdot\boldsymbol{r}')\int d^3r''\;\exp(i\,\boldsymbol{q}\cdot\boldsymbol{r}'')\,\frac{\rho(\boldsymbol{r}')}{r''} \\ &= -\frac{e^2}{4\pi\,\epsilon_0}\,\frac{4\pi}{q^2}\,F(\boldsymbol{q}), \end{aligned} \tag{464}$$

where we have introduced the form factor

$$F(\boldsymbol{q}) = \int d^3r\;\exp(i\,\boldsymbol{q}\cdot\boldsymbol{r})\,\rho(\boldsymbol{r}) \tag{465}$$

which is the Fourier transform of the density. The result for the cross section is

$$\frac{d\sigma}{d\Omega} = \left(\frac{m\,e^2}{2\pi\,\epsilon_0\,\hbar^2\,q^2}\right)^2\frac{p'}{p}\,|F(\boldsymbol{q})|^2\,. \tag{466}$$

and shows the possibility to determine the charge distribution of the system.

In realistic cases the charge density often corresponds to a many-particle system, e.g. an atomic nucleus. In that case one has a charge density for each of the Z positively charged protons, leading to

$$\begin{aligned} \rho_{BA}(\boldsymbol{r}) &= \sum_{j=1}^{Z}\int\prod_{k=1}^{Z} d^3r_k\;\delta^3(\boldsymbol{r}-r_j)\,\Phi_B^*(r_1,\ldots,r_Z)\Phi_A(r_1,\ldots,r_Z) \\ &= Z\int\prod_{k=2}^{Z}\Phi_B^*(r,r_2,\ldots,r_Z)\Phi_A(r,r_2,\ldots,r_Z) = Z\,\rho_{BA}(\boldsymbol{r}). \end{aligned} \tag{467}$$

The second line of this equation could be written down because the wave functions Φ_A and Φ_B are fully antisymmetric under interchange of particles (Pauli principle). The quantity $\rho_{BA}(\boldsymbol{r})$ is called the one-nucleon (transition) density and its Fourier transform is the (transition) form factor $F_{BA}(\boldsymbol{q})$. The effect in the cross section is a factor $Z^2\,|F_{BA}(\boldsymbol{q})|^2$.

One can in turn also include the intrinsic density of the protons, which in the cross section will appear as a multiplicative factor $|F_p(\boldsymbol{q})|^2$, where $F_p(\boldsymbol{q})$ is related to the charge distribution within the proton. Then one should also include the charge densities of the neutrons.

In the case of scattering off an atom one obtains contributions from the atomic nucleus and the electrons. These contributions are additive in the form factor, leading to a contribution in the cross section of the form $Z^2|\delta_{ab} - F_{ba}|^2$.

24.2 Examples of form factors

Form factors as encountered in the previous section are defined as the Fourier transform of a density,

$$F(\boldsymbol{q}) = \int d^3r \ \exp(i\,\boldsymbol{q}\cdot\boldsymbol{r})\,\rho(\boldsymbol{r}). \tag{468}$$

As before in discussing the potential in momentum space, one has for a spherically symmetric density,

$$F(q) = \frac{4\pi}{q}\int dr \ r\,\rho(r)\,\sin(qr). \tag{469}$$

For a spherical distributions it is trivial to find by expanding the exponential $\exp(i\,\boldsymbol{q}\cdot\boldsymbol{r}) = 1 + i\,\boldsymbol{q}\cdot\boldsymbol{r}$ - $\frac{1}{2}\,(\boldsymbol{q}\cdot\boldsymbol{r})^2 + \ldots$, that

$$F(q) = Q - \frac{1}{6}\,q^2\,\langle r^2\rangle + \ldots, \tag{470}$$

where

$$Q = \int d^3r \ \rho(r), \tag{471}$$

$$\langle r^2\rangle = \int d^3r \ r^2\,\rho(r). \tag{472}$$

This is the reason that the small-$\boldsymbol{q}$ behavior of a form factor can be used to determine the charge radius of an atom or similarly of elementary particles, like pions or nucleons.

Some examples of form factors corresponding to specific densities are:

- A uniform density

  $$\rho(r) = \rho_0 \qquad \text{for } x \le R \tag{473}$$

  (and zero elsewhere). If $\rho_0 = 3/4\pi\,a^3$, i.e. the integrated density is one, the Fourier transform is given in terms of the Bessel function j_1,

  $$F(q) = \frac{3\,j_1(qR)}{qR}, \tag{474}$$

  where

  $$j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}. \tag{475}$$

  Note that

  $$\frac{3\,j_1(x)}{x} \approx 1 - \frac{1}{10}\,x^2 + \ldots, \tag{476}$$

  and, indeed, the charge radius of a uniform distribution is $\langle r^2\rangle = \frac{3}{5}\,R^2$.

- A (normalized) Yukawa distribution
  $$\rho(r) = \frac{\mu^2}{4\pi}\,\frac{e^{-\mu r}}{r}, \tag{477}$$
  has as form factor
  $$F(q) = \frac{\mu^2}{q^2+\mu^2} = \frac{1}{1+q^2/\mu^2}, \tag{478}$$
  which is called a *monopole* form factor. We have encountered this example already in a previous section where we derived the momentum space screened Coulomb potential.

- The form factor of the exponential distribution
  $$\rho(r) = \frac{\mu^3}{8\pi}\,e^{-\mu r}, \tag{479}$$
  is simply found by differentiation of the Yukawa form factor with respect to μ,
  $$e^{-\mu r} = -\frac{d}{d\mu}\left(\frac{e^{-\mu r}}{r}\right).$$
  This gives
  $$F(q) = \frac{1}{\left(1+q^2/\mu^2\right)^2}, \tag{480}$$
  which is called a *dipole* form factor.

- Finally a normalized Gaussian distribution
  $$\rho(r) = \rho_0\,e^{-\frac{1}{2}\,r^2/R^2} \tag{481}$$
  has also a Gaussian form factor
  $$F(q) = e^{-\frac{1}{2}\,q^2\,R^2}. \tag{482}$$

Exercises

Exercise 24.1

Give the differential cross section for elastic scattering of an electron off a proton with charge distribution

$$\rho(r) = \frac{e^{-r/R}}{8\pi\,R^3}.$$

with $R = 0.8\times 10^{-15}$ m. Show that the typical value of q at which one notices the composite nature of the proton, implies that the electrons should be ultra-relativistic ($\lambda\!\!\!^{-}_e = \hbar/m_e c \approx 4\times 10^{-13}$ m).

25 Time-independent scattering solutions

25.1 The homogenous solutions

In this section we will attack the scattering of a potential in a different way, namely by solving the Schrödinger equation. The time-independent Schrödinger equation can be rewritten as

$$\left(\boldsymbol{\nabla}^2 + k^2\right)\phi(\boldsymbol{r}) = \frac{2m}{\hbar^2}\,V(\boldsymbol{r})\,\phi(\boldsymbol{r}), \tag{483}$$

where $E = \hbar^2 k^2/2m$. This is a linear equation of which the righthandside is referred to as *source* term. There is a whole family of solutions of such an equation. Given a solution of the above *inhomogeneous* equation, one can obtain all solutions by adding any of the possible solutions of the *homogeneous* equation,

$$\left(\boldsymbol{\nabla}^2 + k^2\right)\phi_{\rm hom}(\boldsymbol{r}) = 0. \tag{484}$$

The solutions of the homogeneous equation are well-known, namely the plane waves,

$$\phi_k(\boldsymbol{r}) = \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}), \tag{485}$$

characterized by a wave vector $\boldsymbol{k}$.

Another systematic way of obtaining the solutions of the homogeneous equation is by considering the radial Schrödinger equation, i.e. writing

$$\phi(\boldsymbol{r}) = \frac{u(r)}{r}\,Y_\ell^m(\theta,\phi), \tag{486}$$

the radial wave function $u(r)$ satisfies for the homogeneous equation

$$\left(\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} + k^2\right)u(r) = 0. \tag{487}$$

There are two type of solutions of this equation

- Regular solutions: spherical Bessel functions of the first kind: $u(r) = kr\,j_\ell(kr)$.
  Properties:

$$\begin{aligned} j_0(z) &= \frac{\sin z}{z}, \\ j_\ell(z) &= z^\ell\left(-\frac{1}{z}\frac{d}{dz}\right)^\ell \frac{\sin z}{z} \quad \overset{z\rightarrow 0}{\longrightarrow} \quad z^\ell, \\ & \qquad\qquad\qquad\qquad\quad \overset{z\rightarrow\infty}{\longrightarrow} \quad \frac{\sin(z-\ell\pi/2)}{z}. \end{aligned}$$

- Irregular solutions: spherical Bessel functions of the second kind: $u(r) = kr\,n_\ell(kr)$.
  Properties:

$$\begin{aligned} n_0(z) &= -\frac{\cos z}{z}, \\ n_\ell(z) &= -z^\ell\left(-\frac{1}{z}\frac{d}{dz}\right)^\ell \frac{\cos z}{z} \quad \overset{z\rightarrow 0}{\longrightarrow} \quad z^{-(\ell+1)}, \\ & \qquad\qquad\qquad\qquad\quad \overset{z\rightarrow\infty}{\longrightarrow} \quad -\frac{\cos(z-\ell\pi/2)}{z}. \end{aligned}$$

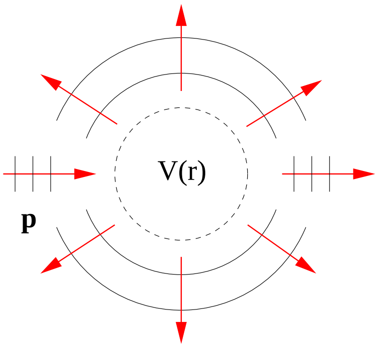
Equivalently one can use linear combinations, known as Hankel functions,

$$
\begin{aligned}
kr\, h_\ell^{(1)}(kr) &= kr\,(j_\ell(kr) + i\, n_\ell(kr)) &\overset{z\to\infty}{\longrightarrow}&\quad (-i)^{\ell+1}\, e^{i\,kr},\\
kr\, h_\ell^{(2)}(kr) &= kr\,(j_\ell(kr) - i\, n_\ell(kr)) &\overset{z\to\infty}{\longrightarrow}&\quad (i)^{\ell+1}\, e^{-i\,kr}.
\end{aligned}
$$

> *A specific example of an expansion into these spherical solutions, is the expansion of the plane wave,*
>
> $$\exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) = e^{i\,kz} = e^{i\,kr\,\cos\theta} = \sum_{\ell=0}^{\infty}(2\ell+1)\,i^\ell\,j_\ell(kr)\,P_\ell(\cos\theta), \tag{488}$$
>
> *where the Legendre polynomials P_ℓ can be also expressed in Y_ℓ^0,*
>
> $$P_\ell(\cos\theta) = \sqrt{\frac{4\pi}{2\ell+1}}\,Y_\ell^0(\theta).$$

25.2 Asymptotic behavior and relation to cross section

In order to construct solutions of the Schrödinger equation that describe a scattering process, one wants the appropriate asymptotic behavior, which includes a plane wave part, describing the incoming part and outgoing spherical waves, describing the scattering part, pictorially represented below



We thus require the following asymptotic form,

$$\phi(\boldsymbol{r}) \quad \overset{r\to\infty}{\longrightarrow} \quad \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) + \frac{e^{i\,kr}}{r}\,f(k;\theta,\phi). \tag{489}$$

We have seen in the previous chapter that for $r\to\infty$, this is a solution of the homogeneous equation.

> *It can also simply be checked that the above represents a solution if $r\to\infty$, by inserting it into the homogeneous equation. In order to select the leading part for large r one needs to use that $\boldsymbol{\nabla} f(k;\theta,\phi) \propto 1/r$ and $\boldsymbol{\nabla}^2 f(k;\theta,\phi) \propto 1/r^2$.*

For the asymptotic solution the current corresponding to the first part is given by

$$\boldsymbol{j}_{in} = \frac{\hbar\boldsymbol{k}}{m}, \tag{490}$$

while the second part up to $\mathscr{O}(1/r)$ corresponds with a radially outward directed flux of magnitude

$$j_r = -\frac{i\hbar}{2m}\left[\phi^*\frac{d}{dr}\phi - \left(\frac{d}{dr}\phi^*\right)\phi\right] = \frac{\hbar k}{m}\,\frac{|f(k;\theta,\phi)|^2}{r^2}. \tag{491}$$

From it, one derives the cross section using that

$$|j_{in}|\,d\sigma(\theta,\phi) = n(\theta,\phi)\,d\Omega = j_r\,r^2\,d\Omega, \tag{492}$$

i.e.

$$\frac{d\sigma}{d\Omega} = |f(k;\theta,\phi)|^2. \tag{493}$$

The above considerations require a careful analysis of the forward direction ($\theta = 0$), where also the interference term becomes important. For an acceptable asymptotic scattering solution one must have that $\int d\Omega\; j_r|_{r=R} = 0$ for large R, i.e. that there is no loss of probability. This leads to the *optical theorem* or Bohr-Peierls-Placzek relation,

$$\mathscr{I}m\, f_{el}(\theta = 0) = \frac{k}{4\pi}\,\sigma_T, \tag{494}$$

where σ_T is the total cross section and f_{el} is the scattering amplitude for elastic scattering.

In order to derive this result, one can just consider the current corresponding to the full wave function in Eq. 489. Keeping only the dominant contributions when $r \to \infty$, this is given by

$$j_r = \frac{\hbar k}{m}\left\{\cos\theta + \frac{|f|^2}{r^2} + \mathscr{R}e\left[(1+\cos\theta)\,\frac{e^{ikr(1-\cos\theta)}}{r}\,f\right]\right\}$$

Integrating over the polar angle (writing $\cos\theta \equiv X$) gives for the interference term:

$$\begin{aligned}
\mathscr{R}e \int_{-1}^{1} dX\;(1+X)\,\frac{e^{i\,kr(1-X)}}{r}\,f
&= \mathscr{R}e \int_{-1}^{1} d\left(e^{i\,kr(1-X)}\right)\,\frac{(1+X)f}{-i\,kr^2} \\
&= \mathscr{R}e\left(\frac{2\,f(k;\theta=0)}{-i\,kr^2}\right) - 2\mathscr{R}e\int_{-1}^{1} dX\;\frac{e^{i\,kr(1-X)}}{-i\,kr^2}\,\frac{d}{dX}\left[(1+X)f\right] \\
&= -\frac{2\,\mathscr{I}m\,f(k;\theta=0)}{kr^2} + \mathscr{O}\left(\frac{1}{r^3}\right).
\end{aligned}$$

The interference term thus actually only contributes at forward angles if $r \to \infty$. Neglecting any contribution disappearing faster than $1/r^2$ the integral over the angles gives

$$\int d\Omega\; j_r\bigg|_{r=R} = \frac{1}{R^2}\left[\int d\Omega\;|f|^2 - \frac{4\pi}{k}\,\mathscr{I}m\,f(k;\theta=0)\right],$$

yielding the optical theorem. In fact the result is only derived if the total cross section is given by the integration over $|f|^2$, but it should be clear that flux conservation needs only to hold if we integrate over elastic and inelastic channels, while the interference only occurs for the elastic channel. We will encounter the result again in the section on partial wave expansions.

25.3 The integral equation for the scattering amplitude

In order to solve the inhomogeneous equation with which we started, we solve the Green's function equation

$$\left(\boldsymbol{\nabla}^2 + k^2\right) G(\boldsymbol{r},\boldsymbol{r}') = -\delta^3(\boldsymbol{r}-\boldsymbol{r}'). \tag{495}$$

> *With the help of the Green's function an inhomogeneous solution for*
>
> $$\left(\boldsymbol{\nabla}^2 + k^2\right)\phi(\boldsymbol{r}) = \rho(\boldsymbol{r}),$$
>
> *can be written down, namely*
>
> $$\phi(\boldsymbol{r}) = \phi_{\rm hom}(\boldsymbol{r}) - \int d^3r'\ G(\boldsymbol{r},\boldsymbol{r}')\,\rho(\boldsymbol{r}').$$
>
> *By choosing an 'appropriate' Green's function one can built in boundary conditions. Note that the difference between any two Green's function is a solution of the homogeneous equation.*

It is possible to check that two particular Green's functions in our case are

$$G^{(\pm)}(\boldsymbol{r}-\boldsymbol{r}') = -\frac{\exp\left(\pm i\,k|\boldsymbol{r}-\boldsymbol{r}'|\right)}{4\pi\,|\boldsymbol{r}-\boldsymbol{r}'|}. \tag{496}$$

Note that the difference between these two is a solution of the homogeneous equation. In particular $G^{(+)}$ has the correct asymptotic behavior as discussed in the previous section. As an *exact*, but implicit, solution valid for all r, we can write

$$\phi(\boldsymbol{r}) = \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) - \frac{m}{2\pi\,\hbar^2}\int d^3r'\ \frac{\exp\left(+i\,k|\boldsymbol{r}-\boldsymbol{r}'|\right)}{|\boldsymbol{r}-\boldsymbol{r}'|}\,V(\boldsymbol{r}')\,\phi(\boldsymbol{r}'). \tag{497}$$

This result is the desired integral representation of the inhomogenous Schrödinger equation, which has the advantages that the boundary conditions for interpretation as a scattering solution have been built in. It is therefore a good starting point for approximations

The result for $f(k;\theta,\phi)$ is obtained by taking the limit for $r\rightarrow\infty$ in the integral equation, in particular

$$|\boldsymbol{r}-\boldsymbol{r}'| = r\sqrt{1 - 2\,\frac{\boldsymbol{r}\cdot\boldsymbol{r}'}{r^2} + \frac{r'^2}{r^2}} \;\approx\; r\left[1 - \frac{\boldsymbol{r}\cdot\boldsymbol{r}'}{r^2} + \ldots\right],$$

$$\frac{\exp\left(+i\,k|\boldsymbol{r}-\boldsymbol{r}'|\right)}{|\boldsymbol{r}-\boldsymbol{r}'|} \;\approx\; \frac{e^{i\,kr}}{r}\,\exp\left(i\,\boldsymbol{k}'\cdot\boldsymbol{r}'\right) + \ldots,$$

where $\boldsymbol{k}' \equiv k\hat{\boldsymbol{r}}$. This gives

$$\phi^{(+)}_{\rm sc}(\boldsymbol{r}) \quad \overset{r\rightarrow\infty}{\longrightarrow} \quad \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) - \frac{e^{i\,kr}}{r}\,\frac{m}{2\pi\,\hbar^2}\int d^3r'\ \exp\left(-i\,\boldsymbol{k}'\cdot\boldsymbol{r}'\right)\ V(\boldsymbol{r}')\,\phi^{(+)}_{\rm sc}(\boldsymbol{r}'). \tag{498}$$

and thus the exact expression is

$$f(k;\theta,\phi) = -\frac{m}{2\pi\,\hbar^2}\int d^3r'\ \exp\left(-i\,\boldsymbol{k}'\cdot\boldsymbol{r}'\right)\ V(\boldsymbol{r}')\,\phi^{(+)}_{\rm sc}(\boldsymbol{r}'). \tag{499}$$

25.4 The Born approximation and beyond

The Born approximation is obtained by using perturbation methods, namely to approximate in the above expression $\phi(\boldsymbol{r}') = \exp\left(i\,\boldsymbol{k}\cdot\boldsymbol{r}'\right)$, yielding the result

$$f(k;\theta,\phi) = -\frac{m}{2\pi\,\hbar^2}\int d^3r'\ \exp\left(i\,\boldsymbol{q}\cdot\boldsymbol{r}'\right)\ V(\boldsymbol{r}'), \tag{500}$$

where $\boldsymbol{q} = \boldsymbol{k}-\boldsymbol{k}'$. This gives for the cross section the same result as we found using Fermi's golden rule.

We can go beyond the first order result by introducing the scattering amplitude T. It is defined by

$$V\phi_{\rm sc}^{(+)} \equiv T\phi,$$

where $\phi_{\rm sc}^{(+)}$ is the scattering solution and ϕ the incoming plane wave part of it. One then finds that the integral equation, $V\phi_{\rm sc}^{(+)} = V\phi + V\,\tilde{G}\,V\phi_{\rm sc}^{(+)}$ turns into $T\phi = V\phi + V\,\tilde{G}\,T\phi$, i.e. an equation for T,

$$T = V + V\,\tilde{G}\,T, \tag{501}$$

the socalled Lippmann-Schwinger *equation. Here $\tilde{G}$ is the Green's function with factor $-2m/\hbar^2$ absorbed, which is the inverse of $E - H_0$. The exact expression for the scattering amplitude f is thus given by*

$$f(k;\theta,\phi) = -\frac{m}{2\pi\,\hbar^2}\,\langle \boldsymbol{p}'|T|\boldsymbol{p}\rangle. \tag{502}$$

The lowest order (Born approximation) result is the first term in the expansion obtained from Eq. 501,

$$T = V + V\,\tilde{G}\,V + V\,\tilde{G}\,V\,\tilde{G}\,V + \ldots.$$

To judge the validity of the Born approximation one requires that the scattering term in the wave function is small, i.e.

$$\frac{m}{2\pi\,\hbar^2}\left|\int d^3r'\;\frac{\exp\left(i\,k|\boldsymbol{r}-\boldsymbol{r}'|\right)}{|\boldsymbol{r}-\boldsymbol{r}'|}\,V(\boldsymbol{r}')\,\phi_{\rm sc}^{(+)}(\boldsymbol{r}')\right| \ll 1. \tag{503}$$

The disturbance of the plane wave is near $r \approx 0$, while for selfconsistency $\phi_{\rm sc}^{(+)}(\boldsymbol{r})$ should be dominantly plane wave, thus

$$\begin{aligned}
&\left|\int d^3r'\;\frac{\exp\left(i\,kr' + i\,\boldsymbol{k}\cdot\boldsymbol{r}'\right)}{r'}\,V(\boldsymbol{r}')\right| \ll \frac{2\pi\,\hbar^2}{m}\\
&\left|2\pi\int_{-1}^{1} dX \int dr'\;r'\,e^{i\,kr'(1+X)}\,V(r')\right| \ll \frac{2\pi\,\hbar^2}{m},\\
&\left|\int dr'\;\left(e^{2i\,kr'} - 1\right)V(r')\right| \ll \frac{\hbar^2 k}{m} = \hbar v.
\end{aligned}$$

We see two limits in which the Born approximation is applicable

- Weak potentials with a finite range.
  Starting with the second of the above estimates, we see for a potential with average depth V_0 and range a one has after bringing the absolute value under the integral $V_0\,a^2 \ll \hbar^2/m$, i.e.

  $$V_0 \ll \frac{\hbar^2}{m\,a^2}, \tag{504}$$

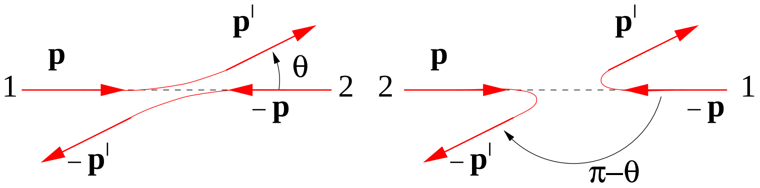
  a condition where an approximately equal sign usually is already ok.

- High energies (but nonrelativistic!).
  In the last of the three expressions the exponential is fast-varying for high momenta k and can be neglected, so $V_0\,a \ll \hbar^2\,k/m$, i.e.

  $$ka \gg \frac{m\,V_0\,a^2}{\hbar^2} \qquad \text{or} \qquad E \gg \frac{m\,V_0^2\,a^2}{\hbar^2}. \tag{505}$$

25.5 Identical particles

We already discussed how to treat the scattering of two particles in the center of mass frame. In the case that one has two identical particles the scattering in the following two situations both leads to the same final state,



Thus if ψ_{12} is the wave function in which particle 1 is coming from the left and is scattered over an angle θ and ψ_{21} is the wave function in which particle 1 is coming from the right and is scattered over an angle $\pi-\theta$,

$$\phi_{12}(\boldsymbol{r}) = e^{i\,kz} + f(k;\theta,\phi)\,\frac{e^{i\,kr}}{r}, \tag{506}$$

$$\phi_{21}(\boldsymbol{r}) = e^{-i\,kz} + f(k;\pi-\theta,\phi+\pi)\,\frac{e^{i\,kr}}{r}, \tag{507}$$

one has the same final state. One should use the appropriately symmetrized or antisymmetrized wave functions, leading to (omitting ϕ-dependence)

$$n(\theta,\phi)\,d\Omega = \frac{\hbar k}{\mu}\,\left|f(k;\theta) \pm f(k;\pi-\theta)\right|^2\,d\Omega$$

In the cross section,

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= \left|f(k;\theta) \pm f(k;\pi-\theta)\right|^2 \\ &= \left|f(k;\theta)\right|^2 + \left|f(k;\pi-\theta)\right|^2 \pm 2\,\mathscr{R}e\left[f^*(k;\theta)\,f(k;\pi-\theta)\right],\end{aligned} \tag{508}$$

the (third) interference term gives rise to oscillations. Note that in order to determine the total cross section one has to integrate over the range $0 \le \theta \le \pi/2$ in order to avoid double counting. Note that the cross sections at angles θ and $\pi-\theta$ are identical. For destructive interference (a minus sign) the cross section is zero at $\theta = 90$ degrees.

For example in the (hypothetical) scattering process of two pions the amplitudes interfere constructively as pions are bosons (spin 0 particles) and the wave function must be symmetric. When scattering two electrons (spin 1/2 particles) off each other the total wave function is antisymmetric, but the symmetry of the scattering solution depends on the spin state. In the spin 0 state (singlet) the spin wave function is antisymmetric, while in the spin 1 state (triplet) the spin wave function is symmetric. Hence

$$\frac{d\sigma_s}{d\Omega} = |f_s(\theta) + f_s(\pi-\theta)|^2, \tag{509}$$

$$\frac{d\sigma_t}{d\Omega} = |f_t(\theta) - f_t(\pi-\theta)|^2, \tag{510}$$

If one scatters unpolarized electrons, the initial state has a probability 1/4 to be in the singlet state, 3/4 to be in the triplet state, thus for a spin-independent potential

$$\frac{d\sigma}{d\Omega} = \frac{1}{4}\,\frac{d\sigma_s}{d\Omega} + \frac{3}{4}\,\frac{d\sigma_t}{d\Omega} = |f(k;\theta)|^2 + |f(k;\pi-\theta)|^2 - \mathscr{R}e\left[f(k;\theta)\,f^*(k;\pi-\theta)\right]. \tag{511}$$

Exercises

Exercise 25.1

In this exercise we look at the ingredients needed to find the Green function in Eq. 495.

(a) Show that

$$\nabla^2 \left(\frac{1}{r}\right) = 0 \quad \text{if } r \neq 0 \qquad \text{and} \qquad \int d^3r\ \nabla^2 \left(\frac{1}{r}\right) = -4\pi,$$

which implies that

$$\nabla^2 \left(\frac{1}{r}\right) = -4\pi\, \delta^3(\boldsymbol{r}).$$

(b) Argue that $G(\boldsymbol{r}, \boldsymbol{r}')$ in Eq. 495 only depends on $\boldsymbol{r} - \boldsymbol{r}'$, thus we have to solve

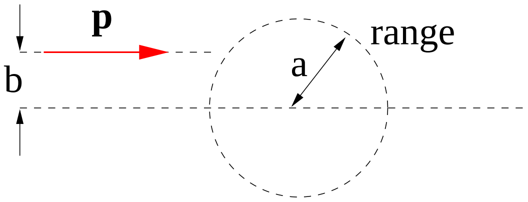
$$\left(\boldsymbol{\nabla}^2 + k^2\right) G(\boldsymbol{r}) = -\delta^3(\boldsymbol{r}).$$

(c) Show that $G(\boldsymbol{r}) = e^{\pm ikr}/4\pi\, r$ is a solution of the equation under (b).

26 Partial wave expansion

26.1 Phase shifts

At low energies a particle scattering off a target with impact parameter b has an angular momentum $\hbar\sqrt{\ell(\ell+1)} = p\, b$,



If the potential has a finite range a the angular momenta that are important correspond to $b \le a$. From this we obtain $\hbar\ell \lesssim pa = \hbar ka$ or $\ell \lesssim ka$. Therefore it is especially at low energies convenient to expand into different partial waves, eigenstates of angular momentum, because the lower partial waves dominate. Also for central potentials, which satisfy $[\boldsymbol{L}, V(r)] = 0$, it is useful to expand in partial waves, since each angular momentum state in that case is a proper scattering solution.

Starting off with the plane wave, we have

$$e^{ikz} = \sum_\ell (2\ell+1)\, i^\ell\, j_\ell(kr)\, P_\ell(\cos\theta). \tag{512}$$

The expansion only contains the ϕ-independent spherical harmonics, $Y_\ell^0(\theta) = \sqrt{(2\ell+1)/4\pi}\, P_\ell(\cos\theta)$. Assuming azimuthal symmetry the scattering amplitude only depends on θ and also can be expanded in Legendre polynomials,

$$f(k;\theta) = \sum_\ell (2\ell+1)\, f_\ell(k)\, P_\ell(\cos\theta). \tag{513}$$

Thus one obtains

$$\phi_{sc}(\boldsymbol{r}) \quad \overset{r\to\infty}{\longrightarrow} \quad \sum_\ell (2\ell+1)\, P_\ell(\cos\theta)\, i^\ell \underbrace{\left[j_\ell(kr) + (-i)^\ell\, \frac{e^{i\,kr}}{r}\, f_\ell(k)\right]}_{\phi_{sc}^{(\ell)}(r)}. \tag{514}$$

Rewriting the scattering wave in the following way,

$$\begin{aligned} \phi_{sc}^{(\ell)}(\boldsymbol{r}) \quad & \overset{r\to\infty}{\longrightarrow} \quad \frac{\sin(kr - \ell\pi/2)}{kr} + (-i)^\ell\, \frac{e^{i\,kr}}{r}\, f_\ell(k) \\ & = \quad \frac{1}{2i\,k}\left[-\frac{e^{-i(kr-\ell\pi/2)}}{r} + \frac{e^{i(kr-\ell\pi/2)}}{r}\,(1 + 2i\,kf_\ell(k))\right], \end{aligned} \tag{515}$$

Conservation of flux tells us that the incoming and outgoing fluxes should be equal in magnitude, i.e.

$$1 + 2i\,kf_\ell(k) \equiv e^{2i\,\delta_\ell(k)}, \tag{516}$$

where $\delta_\ell(k)$ is called the *phase shift*. Going back and expressing $f_\ell(k)$ in the phase shift it is easy to see that

$$f_\ell(k) = \frac{e^{2i\,\delta_\ell(k)} - 1}{2i\,k} = \frac{e^{i\,\delta_\ell(k)}\, \sin\delta_\ell(k)}{k}, \tag{517}$$

and

$$\phi_{sc}^{(\ell)}(\boldsymbol{r}) \quad \overset{r\to\infty}{\longrightarrow} \quad e^{i\,\delta_\ell(k)}\, \frac{\sin(kr - \ell\pi/2 + \delta_\ell(k))}{kr}. \tag{518}$$

26.2 Cross sections and partial waves

At this point it is useful to slightly generalize the result of the previous section. If also inelastic scattering is possible a particular ℓ-wave amplitude is parametrized

$$1 + 2i\,k f_\ell(k) \equiv \eta_\ell\, e^{2i\,\delta_\ell(k)}, \tag{519}$$

where η_ℓ is called the *elasticity.* One then has for the elastic cross section

$$\frac{d\sigma_{el}}{d\Omega} = |f(k;\theta)|^2 = 4\pi \sum_{\ell,\ell'} \sqrt{(2\ell+1)(2\ell'+1)}\, f_\ell(k)\, f_{\ell'}(k)\, Y_\ell^{0*}(\theta)\, Y_{\ell'}^0(\theta). \tag{520}$$

Integrating over angles the orthonormality of the Y_ℓ^m's can be used to get

$$\sigma_{el} = \frac{4\pi}{k^2} \sum_\ell (2\ell+1)\,\sin^2\delta_\ell(k) \tag{521}$$

Via the optical theorem, which relates the forward scattering amplitude to the total cross section one finds

$$\sigma_T = \frac{2\pi}{k^2} \sum_\ell (2\ell+1)\,(1 - \eta_\ell\,\cos 2\delta_\ell), \tag{522}$$

which indeed is identical for purely elastic scattering ($\eta_\ell = 1$). The difference is the inelastic cross section,

$$\sigma_{inel} = \frac{\pi}{k^2} \sum_\ell (2\ell+1)\,(1 - \eta_\ell^2). \tag{523}$$

26.3 Application: the phase shift from the potential

The easiest illustration of the calculation of the phase shift is the calculation for a square well, $V(r) = V_0$ for $r \le a$ and zero elsewhere. We immediately know that for $r \ge a$ the solution must be the asymptotic solution. Inside the square well we use the radial Schrödinger equation to get the radial wave function $u(r)$. Thus for

$$\phi_{\ell m}(\boldsymbol{r}) = \frac{u_\ell(r)}{r}\, Y_\ell^m(\theta,\phi), \tag{524}$$

we have

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} + V(r)\right] u_\ell(r) = E\, u_\ell(r). \tag{525}$$

Knowing that $u_\ell(0) = 0$ we obtain for s-waves ($\ell = 0$)

$$\begin{aligned} &r \le a \qquad u(r) = A\,\sin Kr \qquad \text{with } K = \sqrt{\frac{2m}{\hbar^2}\,(E - V_0)},\\ &r \ge a \qquad u(r) = B\,\sin(kr + \delta_0) \quad \text{with } k = \sqrt{\frac{2m}{\hbar^2}\,E}, \end{aligned}$$

Matching the logarithmic derivative $(du/dr)/u(r)$ at $r = a$ gives

$$\tan(ka + \delta_0) = \frac{k}{K}\,\tan Ka \tag{526}$$

or

$$\tan\delta_0(k) = \frac{\frac{k}{K}\,\tan Ka - \tan ka}{1 + \frac{k}{K}\,\tan Ka\,\tan ka} \tag{527}$$

$$\xrightarrow{ka \ll 1} \frac{ka\left[\frac{\tan Ka}{Ka} - 1\right]}{1 + (ka)^2\,\frac{\tan Ka}{Ka}}, \tag{528}$$

$$\xrightarrow{Ka \ll 1} ka\left[\frac{\tan Ka}{Ka} - 1\right] \approx \frac{K^2\,a^3}{3}\,k \tag{529}$$

For low energies, where s-waves are the dominant contribution, the above result and its limits can be used to understand many qualitative features in the cross section, e.g. the disappearance of the cross section at specific energies, because of a zero in $1 - \tan Ka/Ka$ (the Ramsauer-Townsend effect) or the behavior of the cross section near threshold for weak potentials. The first two coefficients of the phase shift in an expansion in the momentum,

$$\delta_0(k) = a_0\,k + \frac{1}{2}\,r_e\,k^2 + \ldots, \tag{530}$$

have specific names, namely *scattering length* and *effective range*, respectively.

Exercises

Exercise 26.1

Determine the s-wave phase shift for a hard core potential of the form $V(r) = \infty$ for $r \leq b$ and $V(r) = 0$ else.

Exercise 26.2

(a) Determine the phase shift for a potential of the form

$$\begin{aligned} V(r) &= 0 \quad \text{for } r \leq a, \\ &= +V_0 \quad \text{for } a < r \leq b, \\ &= 0 \quad \text{for } r > b. \end{aligned}$$

(b) Write down and plot the s-wave contribution to the cross section for $4m\,V_0\,a^2 = 4\pi^2\,\hbar^2$ and $b = 2\,a$.

Exercise 26.3

We now look at a potential of the form $V(r) = V_0\,a\,\delta(r - a)$, which represents a 'sharp' wall at $r = a$. Determine the s-wave phase shift for this potential.