Advanced Quantum Mechanics

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Lecture notes for the academic year 2012-2013

Preface

The lectures Advanced Quantum Mechanics in the fall semester 2012 will be taught by Piet Mulders. We will be using a few books, depending on the choice of topics. For the basis we will use these lecture notes and the books *Introduction to Quantum Mechanics, second edition* by D.J. Griffiths (Pearson) and *Quantum Mechanics; second edition* by B.H. Bransden and C.J. Joachain (Prentice Hall). The course is for 6 credits and is given fully in period 1. This means that during this period you will need to work on this course 50% of your study time. The lectures will be given on Tuesday and Thursday mornings from 10.00 a.m. to 12.45 with the problem sessions and discussions integrated.

Piet Mulders
September 2012

Schedule (indicative, to be completed later)

	Notes	Books	Remarks
Week 36	1, 2, 3	G 1 - 3	
	4, 5	G 5.3, 4.1 - 4.3	
Week 37	6	G 4.4	
	7	G CT X, p. 999-1058	
Week 38	8	G 5	
	9	G 5	
Week 39	10, 11	G 6	
	12	G 7	
Week 40	13, 14	G 9	
	15, 16	G 10	
Week 41	17, 18	G 11	
	19, 20	G 11, BJ 15	
Week 42	21, 22	BJ 15	

Literature: Useful books are

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

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1 Basics in quantum mechanics

At this point, you should be familiar with the basic aspects of quantum mechanics. That means you should be familiar with working with operators, in particular position and momentum operators that do not commute, but satisfy the basic commutation relation

$$[r_i, p_j] = i\hbar\,\delta_{ij}. \tag{1}$$

The most common way of working with these operators is in an explicit Hilbert space of square integrable (complex) wave functions $\psi(\boldsymbol{r}, t)$ in which operators just produce new functions ($\psi \to \psi' = O\psi$). The position operator produces a new function by just multiplication with the position (argument) itself. The momentum operator acts as a derivative, $\boldsymbol{p} = -i\hbar\,\boldsymbol{\nabla}$, with the appropriate factors such that the operator is hermitean and the basic commutation relation is satisfied. We want to stress at this point the non-observability of the wave function. It are the operators and their eigenvalues as outcome of measurements that are relevant. As far as the Hilbert space is concerned, one can work with any appropriate basis. This can be a finite basis, for example the two spin states along a specified direction for a spin 1/2 particle or an infinite dimensional basis, for example the position or momentum eigenstates. In general a basis is a set of *eigenstates* of one or more operators, denoted by a bra in Dirac representation containing the (relevant) eigenvalues as quantum states. Here the kets must contain a set of 'good' quantum numbers, i.e. a number of eigenvalues of compatible (commuting) operators.

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Question: Why is it essential that the quantum numbers within *one* ket correspond to eigenvalues of *commuting* operators?

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The connection with wave functions uses the (formal) eigenstates of position *or* momentum operators, $|\boldsymbol{r}\rangle$ or $|\boldsymbol{p}\rangle$. The coordinate state wave function then is just the overlap of states given by the inner product in Hilbert space, $\phi(\boldsymbol{r}) = \langle \boldsymbol{r}|\phi\rangle$, of which the square gives the probability to find a state $|\phi\rangle$ in the state $|\boldsymbol{r}\rangle$. Similarly one has the momentum state wave function, $\tilde{\phi}(\boldsymbol{p}) = \langle \boldsymbol{p}|\phi\rangle$.

Some operators can be constructed from the basic operators such as the angular momentum operator $\boldsymbol{\ell} = \boldsymbol{r} \times \boldsymbol{p}$ with components $\ell_i = \epsilon_{ijk}\, r_j p_k$. The most important operator in quantum mechanics is the Hamiltonian. It determines the time evolution to be discussed below. The Hamiltonian $H(\boldsymbol{r}, \boldsymbol{p}, \boldsymbol{s}, \ldots)$ may also contain operators other than those related to space ($\boldsymbol{r}$ and $\boldsymbol{p}$). These correspond to specific properties, such as the spin operators, satisfying the commutation relations

$$[s_i, s_j] = i\hbar\,\epsilon_{ijk}\, s_k. \tag{2}$$

In non-relativistic quantum mechanics all spin properties of systems are 'independent' from spatial properties, which at the operator level means that spin operators commute with the position and momentum operators. As a reminder, this implies that momenta and spins can be specified simultaneously (compatibility of the operators). The spin states are usually represented as spinors (column vectors) in an abstract spin-space, which forms a linear space over the complex numbers.

The most stunning feature of quantum mechanics is the possibility of superposition of quantum states. This property is of course the basic requisite for having a description in terms of a linear space over the complex numbers $\mathbb{C}$.

2 Concepts of quantum mechanics

2.1 The Hilbert space

In quantum mechanics the degrees of freedom of classical mechanics become operators acting in a Hilbert space $\mathscr{H}$, which is a linear space of quantum states, denoted as *kets* $|u\rangle$. These form a linear vector space over the complex numbers ($\mathbb{C}$), thus a combination $|u\rangle = c_1|u_1\rangle + c_2|u_2\rangle$ also satisfies $|u\rangle \in \mathscr{H}$. Having a linear space we can work with a complete basis of linearly independent kets, $\{|u_1\rangle, \ldots, |u_1\rangle\}$ for an N-dimensional Hilbert-space, although N in many quantum mechanical applications certainly can be infinite! An operator A acts as a mapping in the Hilbert-space $\mathscr{H}$, i.e. $|v\rangle = A|u\rangle = |Au\rangle \in \mathscr{H}$. Most relevant operators are linear, if $|u\rangle = c_1|u_1\rangle + c_2|u_2\rangle$ then $A|u\rangle = c_1\,A|u_1\rangle + c_2\,A|u_2\rangle$.

It is important to realize that operators in general do not commute. One defines the commutator of two operators as $[A, B] \equiv AB - BA$. We already mentioned the commutator of position and momentu-moperators, satisfying

$$[\hat{x}_i, \hat{x}_j] = [\hat{p}_i, \hat{p}_j] = 0 \quad \text{and} \quad [\hat{x}_i, \hat{p}_j] = i\hbar\,\delta_{ij}, \tag{3}$$

The commutator is a bilinear product and satisfies

- $[A, B] = -[B, A]$
- $[A, BC] = [A, B]C + B[A, C]$ (Leibniz identity)
- $[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$ (Jacobi identity),
- $[f(A), A] = 0$.

The last property follows assuming that 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 $[A^n, A] = A^nA - AA^n = 0$.

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Exercise: Use the above relations to show some or all examples below of commutators

$$\begin{aligned}
&[\ell_i, \ell_j] = i\hbar\,\epsilon_{ijk}\,\ell_k \quad \text{and} \quad [\boldsymbol{\ell}^2, \ell_i] = 0,\\
&[\ell_i, r_j] = i\hbar\,\epsilon_{ijk}\,r_k \quad \text{and} \quad [\ell_i, p_j] = i\hbar\,\epsilon_{ijk}\,p_k,\\
&[\ell_i, \boldsymbol{r}^2] = 0, \quad [\ell_i, \boldsymbol{p}^2] = 0 \quad \text{and} \quad [\ell_i, \boldsymbol{p}\cdot\boldsymbol{r}] = 0,\\
&[p_i, \boldsymbol{r}^2] = -2\,i\hbar\,r_i, \quad [r_i, \boldsymbol{p}^2] = 2\,i\hbar\,p_i, \quad \text{and} \quad [p_i, V(\boldsymbol{r})] = -i\hbar\,\nabla_i V.
\end{aligned}$$

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Quantum states

Within the Hilbert space, one constructs the inner product of two states. For elements $|u\rangle$, $|v\rangle \in \mathscr{H}$ the inner product is defined as 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 $\langle v|u\rangle = c_1\langle v|u_1\rangle + c_2\langle v|u_2\rangle$,
- $\langle u|u\rangle \geq 0$.

The second property implies $\langle u|v\rangle = \langle v|u\rangle^* = c_1^*\langle v|u_1\rangle^* + c_2^*\langle v|u_2\rangle^* = c_1^*\langle u_1|v\rangle + c_2^*\langle u_2|v\rangle$. Beside the ket-space we can also introduce the dual bra-space, $\mathscr{H}^* = \{\langle u|\}$, which is anti-linear meaning that

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

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

With the help of the inner product, we can define *normalized* states, $\langle u|u\rangle = 1$ and *orthogonal* states satisfying $\langle u|v\rangle = 0$. In a linear vector space an orthonormal basis $\{|u_1\rangle, |u_2\rangle, \ldots\}$ with $\langle u_m|u_n\rangle = \delta_{mn}$ can be constructed. Every state can be expanded in the basis. Using the orthonormal basis, we can easily find the expansion coefficients

$$|u\rangle = \sum_n c_n|u_n\rangle \quad \text{with} \quad c_n = \langle u_n|u\rangle \tag{4}$$

and we can write

$$|u\rangle = \sum_n |u_n\rangle \underbrace{\langle u_n|u\rangle}_{c_n} \equiv \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}. \tag{5}$$

Note that $\langle u|u\rangle = 1$ implies $\sum_n |c_n|^2 = 1$, hence the name *probability amplitude* for c_n and *probability* for the squared amplitude $|c_n|^2$.

2.2 Operators in Hilbert space: observables and measurements

One of the pecularities of quantum mechanics is the role of measurements. Which quantities are measurable? In quantum mechanics it turns out that a measurement performed on a system characterized by a particular state in general does not give a unique answer. But immediately repeating the measurement it does give the same result. Performing another type of measurement in general again gives more possibilities for the outcome. The way it works in quantum mechanics where observables correspond with operators requires considering the *eigenvalues* and *eigenstates* of the operator A, defined as

$$A|a_n\rangle = a_n|a_n\rangle. \tag{6}$$

Here the $|a_n\rangle$ is referred to as the eigenstate belonging to the eigenvalue a_n. In general a system is in a state $|u\rangle$, which is not necessarily an eigenstate of A, but it can be expanded in eigenstates $|a_n\rangle$ as $|u\rangle = \sum_n c_n|a_n\rangle$. Performing a measurement of an observable A then gives one of the eigenvalues a_n with a probability $|c_n|^2$ and leaves the system in the corresponding eigenstate $|a_n\rangle$, schematically represented as

$$\text{state before} \rightarrow \boxed{\text{measurement}} \rightarrow \text{outcome and probability} \rightarrow \text{state after.}$$

$$|u\rangle \quad \rightarrow \quad \boxed{\hat{A}} \quad \rightarrow \begin{cases} \rightarrow \vdots \\ \rightarrow \ a_n \qquad \text{Prob} = |c_n|^2 \quad \rightarrow \quad |a_n\rangle \\ \rightarrow \vdots \end{cases}$$

After the measurement (yielding e.g. a_1 the system is in the eigenstate $|a_1\rangle$ belonging to that eigenvalue (or a linear combination of states if there is degeneracy, i.e. if there are more states with the same eigenvalue). This postulate has wide implications.

There are a few points to keep in mind about the operators. We mostly have operators with real eigenvalues, which implies *hermitean* operators (see below). The collection of eigenvalues $\{a_n\}$ is referred to as the *spectrum of an operator*. It can be discrete or continuous. For example for the momentum operator $\hat{p}_x$ the eigenstates $|\phi_k\rangle$ are the functions $\phi_k(x) = \exp(i\,kx)$ with eigenvalues $\hbar k$ taking any real value. For the angular momentum operator $\hat{\ell}_z$ the eigenfunctions are $\phi_m(\varphi) = \exp(i\,m\varphi)$ with eigenvalues $m\hbar$ with $m \in \mathbb{Z}$. The full set of eigenstates of an hermitean operator actually forms a basis of the Hilbert space, so one can expand any state.

Expectation values and matrix mechanics

To formalize some of the results it is useful to consider in general the matrix elements of (usually linear) operators $\langle u|A|v\rangle$. which is referred to as the matrix element of A between states $|u\rangle$ and $|v\rangle$. It is the inner product of the states $A|v\rangle$ and $|u\rangle$. If $|u\rangle = |v\rangle$ we call this the *expectation value* of A, if $|u\rangle \neq |v\rangle$ we refer to it as *transition matrix element*. Using any orthonormal basis of states, one can write the operators as matrices, 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 $A|u\rangle$

$$\begin{aligned} A|u\rangle &= \sum_n A|u_n\rangle\langle u_n|u\rangle \\ &= \sum_{m,n} |u_m\rangle \underbrace{\langle u_m|A|u_n\rangle}_{A_{mn}} \underbrace{\langle u_n|u\rangle}_{c_n} = \sum_m |u_m\rangle \left(\sum_n A_{mn}c_n\right) \\ &= \begin{pmatrix} A_{11} & A_{12} & \dots \\ A_{21} & A_{22} & \dots \\ \vdots & \vdots & \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}. \end{aligned} \tag{7}$$

With $|v\rangle = \sum_n d_n|u_n\rangle$, matrix element of A is given by

$$\begin{aligned} \langle v|A|u\rangle &= \sum_{m,n} \underbrace{\langle v|u_m\rangle}_{d_m^*} \underbrace{\langle u_m|A|u_n\rangle}_{A_{mn}} \underbrace{\langle u_n|u\rangle}_{c_n} \\ &= (d_1^* \; d_2^* \; \dots) \begin{pmatrix} A_{11} & A_{12} & \dots \\ A_{21} & A_{22} & \dots \\ \vdots & \vdots & \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} \end{aligned} \tag{8}$$

The matrix elements between basis states thus are precisely the entries in the matrix, of which each column gives the image of a basis state.

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

$$I = \sum_n |u_n\rangle\langle u_n|, \tag{9}$$

directly following from Eq. 5 and known as *completeness relation*

Hermitean operators

The Hamiltonian and many other operators (like position and momentum operators) used in quantum mechanics are hermitean operators. Besides real eigenvalues, the eigenstates form a complete set of eigenstates. To formalize some of the aspects of hermitean operators, first look at the adjoint operator $A^\dagger$, which is defined by giving its matrix elements in terms of those of the operator A,

$$\langle u|A^\dagger|v\rangle \equiv \langle v|A|u\rangle^* = \langle v|Au\rangle^* = \langle Au|v\rangle. \tag{10}$$

Thus note that de bra-state $\langle Au| = \langle u|A^\dagger$. In matrix language one thus has that $A^\dagger = A^{T*}$. An operator A is hermitean when expectation values are real, thus

$$\langle u|Au\rangle = \langle u|Au\rangle^* = \langle Au|u\rangle. \tag{11}$$

By applying this to a state $c_1|u\rangle + c_2|v\rangle$ with arbitrary coefficients one sees that for a linear operator this definition is equivalent with $\langle u|Av\rangle = \langle Au|v\rangle$ which can be also written as $\langle u|A|v\rangle = \langle u|A^\dagger|v\rangle$, thus $A = A^\dagger$, i.e. A is self-adjoint.

Now consider the eigenstates $|a_n\rangle$ of a hermitean operator A, i.e. $A|a_n\rangle = a_n|a_n\rangle$. For the eigenvalues (a_n) and eigenstates $(|a_n\rangle)$, of a hermitean operator we have some important properties,

- Normalizing the eigenstates, one sees that $\langle a_n|A|a_n\rangle = a_n$ are the (real) eigenvalues.
- Eigenstates corresponding with nondegenerate eigenvalues are orthogonal,

  $$\text{If } A|a_n\rangle = a_n|a_n\rangle \text{ and } A|a_m\rangle = a_m|a_m\rangle \text{ and } a_m \neq a_n \text{ then } \langle a_m|a_n\rangle = 0.$$

  If eigenvalues are degenerate, we can construct orthogonal eigenstates within the subspace of degenerate eigenstates using straightforward orthogonalization known from linear algebra.
- Thus, eigenstates can be choosen as an orthonormal basis, $\langle a_m|a_n\rangle = \delta_{mn}$. Using this basis A is diagonal,

  $$A = \sum_n |a_n\rangle a_n \langle a_n| = \begin{pmatrix} a_1 & 0 & \dots \\ 0 & a_2 & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}. \tag{12}$$

We can now express the expectation value of a hermitean operator as

$$\langle u|A|u\rangle = \sum_n \underbrace{\langle u|a_n\rangle}_{c_n^*} a_n \underbrace{\langle a_n|u\rangle}_{c_n} = \sum_n a_n |c_n|^2. \tag{13}$$

This shows that the *expectation value* of an operator in a state $|u\rangle$ is the average outcome of measuring the observable A. The quantity $|c_n|^2$ is the probability to find the state $|a_n\rangle$ and obtain the result a_n in a measurement as in the scheme above.

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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.

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Unitary operators

Useful operators in quantum mechanics are also the unitary operators. 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 the scalar products,

$$\langle Uv|Uw\rangle = \langle v|w\rangle \tag{14}$$

With a unitary matrix we can transform an orthonormal basis $\{|u_i\rangle\}$ in another such basis $\{U|u_i\rangle\}$. As a matrix the states $U|u_i\rangle$ are the columns of a matrix, which are normalized and orthogonal to each other. Since also $U^{-1} = U^\dagger$ is unitary, also the rows are normalized and orthogonal to each other. In general, we can diagonalize a hermitean matrix with unitary matrices,

$$\langle u_i|A|u_j\rangle = \sum_n \langle u_i|a_n\rangle a_n \langle a_n|u_j\rangle \quad \text{or} \quad A = S\, A_{\text{diag}} S^\dagger. \tag{15}$$

where S is the matrix that has the eigenstates $|a_n\rangle$ as columns and A_{diag} is the matrix with eigenvalues on the diagonal (Eq. 12).

Coordinate and momentum representation

Coordinate and momentum operators can also be treated along the lines above, which provides the link between *wave quantum mechanics* (Schrödinger) and *matrix quantum mechanics* (Heisenberg). 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. Using position eigenstates $|\boldsymbol{r}\rangle$ satisfying $\hat{\boldsymbol{r}}|\boldsymbol{r}\rangle = \boldsymbol{r}|\boldsymbol{r}\rangle$ one writes operators

$$I = \int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle\langle\boldsymbol{r}| \quad \text{and} \quad \hat{\boldsymbol{r}} = \int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle\boldsymbol{r}\langle\boldsymbol{r}|. \tag{16}$$

and expands any state as

$$|\psi\rangle = \int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle\langle\boldsymbol{r}|\psi\rangle \equiv \int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle\,\psi(\boldsymbol{r}) \tag{17}$$

in which $\psi(\boldsymbol{r}) \in \mathbb{C}$ is the *coordinate space* wave function. The form of the unit operator also fixes the normalization,

$$\langle\boldsymbol{r}|\boldsymbol{r}'\rangle = \delta^3(\boldsymbol{r} - \boldsymbol{r}'), \tag{18}$$

which is also the coordinate space wave function for $|\boldsymbol{r}'\rangle$.

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Exercise: Check that $\hat{\boldsymbol{r}}\psi(\boldsymbol{r}) = \boldsymbol{r}\,\psi(\boldsymbol{r})$ with the above definition of $\psi(\boldsymbol{r})$.

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Exercise: Similarly use the unit operator to express the scalar products $\langle\psi|\psi\rangle$ and $\langle\phi|\psi\rangle$ as integrals over $\psi(\boldsymbol{r})$ and $\phi(\boldsymbol{r})$.

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In the coordinate representation the momentum operator is given by

$$\hat{\boldsymbol{p}} = \int d^3\boldsymbol{r}\ |\boldsymbol{r}\rangle\,(-i\hbar\boldsymbol{\nabla})\,\langle\boldsymbol{r}|, \tag{19}$$

which is identical to $\boldsymbol{p} = -i\hbar\boldsymbol{\nabla}$ in the space of wave functions, obeying $[\hat{r}_i, \hat{p}_j] = i\hbar\,\delta_{ij}$. Knowing the function $\phi_p(\boldsymbol{r})$ translates for the momentum eigenstate $|\boldsymbol{p}\rangle$ into

$$\langle\boldsymbol{r}|\boldsymbol{p}\rangle = \sqrt{\rho}\,\exp\left(i\,\boldsymbol{p}\cdot\boldsymbol{r}/\hbar\right). \tag{20}$$

This defines ρ, e.g. in a box $\rho = 1/L^3$, which is in principle arbitrary. Quite common choices for the normalization of plane waves are $\rho = 1$ or $\rho = (2\pi\hbar)^{-3}$ (non-relativistic) or $\rho = 2E$ (relativistic). The quantity ρ also appears in the normalization of the momentum eigenstates,

$$\langle\boldsymbol{p}|\boldsymbol{p}'\rangle = \rho\,(2\pi\hbar)^3\,\delta^3(\boldsymbol{p} - \boldsymbol{p}'). \tag{21}$$

Using for momentum eigenstates $\hat{\boldsymbol{p}}|\boldsymbol{p}\rangle = \boldsymbol{p}|\boldsymbol{p}\rangle$ one has with the above normalization,

$$I = \int \frac{d^3p}{(2\pi\hbar)^3\,\rho}\ |\boldsymbol{p}\rangle\langle\boldsymbol{p}| \quad \text{and} \quad \hat{\boldsymbol{p}} = \int \frac{d^3p}{(2\pi\hbar)^3\,\rho}\ |\boldsymbol{p}\rangle\boldsymbol{p}\langle\boldsymbol{p}|. \tag{22}$$

The expansion of a state

$$|\psi\rangle = \int \frac{d^3p}{(2\pi\hbar)^3\,\rho}\ |\boldsymbol{p}\rangle\,\langle\boldsymbol{p}|\psi\rangle \equiv \int \frac{d^3p}{(2\pi\hbar)^3\,\rho}\ |\boldsymbol{p}\rangle\,\tilde{\psi}(\boldsymbol{p}) \tag{23}$$

defines the momentum space wave function, which is the Fourier transform of the coordinate space wave function.

2.3 Stationary states

A special role is played by the eigenvalues and eigenstates of the Hamiltonian, which is built from other operators, but also describes time evolution. When the Hamiltonian is independent of time itself and has a set of (time-independent) eigenfunctions,

$$H\phi_n = E_n\phi_n. \tag{24}$$

the eigenvalues define the *energy spectrum* of the system. The eigenstates are referred to as stationary states, Since the Hamiltonian also describes the time evolution, $H = i\hbar\,\partial/\partial t$ we obtain the time-dependent solution,

$$\psi_n(t) = \phi_n\, e^{-i\,E_n t/\hbar}, \tag{25}$$

Depending on the starting point at time $t = 0$ a non-disturbed system evolves as a stationary state or a superposition of stationary states. If $\psi(0) = \phi_n$ then $\psi(t)$ is given by Eq. 25, but

$$\text{if } \psi(0) = \sum_n c_n\,\phi_n \quad \text{then} \quad \psi(t) = \sum_n c_n(t)\,\phi_n = \sum_n c_n\,\phi_n\, e^{-iE_n t/\hbar}. \tag{26}$$

In general the resulting state $|a_n\rangle$ after a measurement of A as discussed above is not an eigenstate of H, and one must re-expand it in energy eigenstates to find its further time evolution. Doing another measurement at a later time then again requires expansion of the time-evolved state in eigenstates of A.

2.4 Compatibility of operators and commutators

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_{abr}, labeled by the eigenvalues of A, B and possibly an index r in case of degeneracy. Thus $A\,\psi_{abr} = a\,\psi_{abr}$ and $B\,\psi_{abr} = b\,\psi_{abr}$. Suppose we have an arbitrary state $\psi = \sum_{abr} c_{abr}\,\psi_{abr}$, then we see that measurements of A and B or those in reverse order yield similar results,

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

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

Compatible operators can be readily identified using the following theorem:

$$A \text{ and } B \text{ are compatible } \iff [A,B] = 0. \tag{27}$$

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 spherical harmonics $Y_m^\ell(\theta,\varphi)$ are the common set of eigenfunctions.

The uncertainty relations

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.
The product of the standard deviations is bounded, depending on the commutator.

The precise bound on the product is given by

$$\Delta A\,\Delta B \geq \frac{1}{2}|\langle\,[A,B]\,\rangle|, \tag{28}$$

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 (why), $\langle\gamma\rangle$ 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

$$\Delta x\,\Delta p_x \geq \frac{1}{2}\,\hbar. \tag{29}$$

Constants of motion

The time-dependence of an expectation value and the correspondence with classical mechanics is often used to find the candidate momentum operator in quantum mechanics. We now take a more general look at this and write

$$\begin{aligned}\frac{d\langle A\rangle}{dt} &= \frac{d}{dt}\int d^3r\;\psi^*(\boldsymbol{r},t)A\psi(\boldsymbol{r},t) = \int d^3r\;\left[\frac{\partial\psi^*}{\partial t}\,A\psi + \psi^*\,A\frac{\partial\psi}{\partial t} + \psi^*\,\frac{\partial A}{\partial t}\,\psi\right]\\ &= \frac{1}{i\hbar}\,\langle\,[A,H]\,\rangle + \langle\frac{\partial}{\partial t}A\rangle.\end{aligned} \tag{30}$$

Examples of this relation are the Ehrenfest relations

$$\frac{d}{dt}\,\langle\boldsymbol{r}\rangle = \frac{1}{i\hbar}\,\langle[\boldsymbol{r},H]\rangle = \frac{1}{i\hbar}\,\frac{1}{2m}\,\langle[\boldsymbol{r},\boldsymbol{p}^2]\rangle = \frac{\langle\boldsymbol{p}\rangle}{m}, \tag{31}$$

$$\frac{d}{dt}\,\langle\boldsymbol{p}\rangle = \frac{1}{i\hbar}\,\langle[\boldsymbol{p},H]\rangle = \frac{1}{i\hbar}\,\langle[\boldsymbol{p},V(\boldsymbol{r})]\rangle = \langle-\boldsymbol{\nabla}V(\boldsymbol{r})\rangle. \tag{32}$$

An hermitean operator A that is compatible with the Hamiltonian, i.e. $[A,H]=0$ and that does not have explicit time dependence, i.e. $\frac{\partial A}{\partial t} = 0$ is referred to as a *constant of motion*. From Eq. 30 it is clear that its expectation value is time-independent.

==========

Exercise: Check the following examples of constants of motion, compatible with the Hamiltonian and thus providing eigenvalues that can be used to label eigenfunctions of the Hamiltonian.

(a) The hamiltonian for a free particle

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

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

(b) 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 $\phi_{n\ell m}(\boldsymbol{r}) = (u(r)/r)\, Y_m^\ell(\theta,\varphi)$.

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3 Concepts in classical mechanics

3.1 Euler-Lagrange equations

Starting with positions and velocities, Newton's equations in the form of a force that gives a change of momentum, $\boldsymbol{F} = d\boldsymbol{p}/dt = d(m\dot{\boldsymbol{r}})/dt$ can be used to solve many problems. Here momentum including the mass m shows up. One can extend it to several masses or mass distributions in which $m = \int d^3x\, \rho(\boldsymbol{r})$, where density and mass might itself be time-dependent. In several cases the problem is made easier by introducing other coordinates, such as center of mass and relative coordinates, or using polar coordinates. Furthermore many forces are conservative, in which case they can be expressed as $\boldsymbol{F} = -\boldsymbol{\nabla} V$.

In a system with several degrees of freedom $\boldsymbol{r}_i$, the forces in $\boldsymbol{F}_i - m\ddot{\boldsymbol{r}}_i$ may contain internal constraining forces that satisfy $\sum_i \boldsymbol{F}_i^{\rm int} \cdot \delta\boldsymbol{r}_i = 0$ (no work). This leads to D'alembert's principle,

$$\sum_i \left(\boldsymbol{F}_i^{\rm ext} - m\ddot{\boldsymbol{r}}_i\right) \cdot \delta\boldsymbol{r}_i = 0. \tag{33}$$

This requires the sum, because the variations $\delta\boldsymbol{r}_i$ are not necessarily independent. Identifying the truly independent variables,

$$\boldsymbol{r}_i = \boldsymbol{r}_i(q_\alpha, t), \tag{34}$$

with i being any of $3N$ coordinates of N particles and α running up to $3N - k$ where k is the number of constraints. The true path can be written as a variational principle,

$$\int_{t_1}^{t_2} dt\ \sum_i \left(\boldsymbol{F}_i^{\rm ext} - m\ddot{\boldsymbol{r}}_i\right) \cdot \delta\boldsymbol{r}_i = 0, \tag{35}$$

or in terms of the independent variables as a variation of the action between fixed initial and final times,

$$\delta S(t_1, t_2) = \delta \int_{t_1}^{t_2} dt\ L(q_\alpha, \dot{q}_\alpha, t) = 0. \tag{36}$$

The solution for variations in q_α and $\dot{q}_\alpha$ between endpoints is

$$\begin{aligned} \delta S &= \int_{t_1}^{t_2} dt \sum_\alpha \left(\frac{\partial L}{\partial q_\alpha}\,\delta q_\alpha + \frac{\partial L}{\partial \dot{q}_\alpha}\,\delta\dot{q}_\alpha\right) \\ &= \int_{t_1}^{t_2} dt \sum_\alpha \left(\frac{\partial L}{\partial q_\alpha} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}_\alpha}\right)\delta q_\alpha + \sum_\alpha \frac{\partial L}{\partial \dot{q}_\alpha}\delta q_\alpha\Bigg|_{t_1}^{t_2} \end{aligned} \tag{37}$$

which because of the independene of the δq_α's gives the Euler-Lagrange equations

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_\alpha} = \frac{\partial L}{\partial q_\alpha}. \tag{38}$$

For a simple unconstrained system of particles in an external potential, one has

$$L(\boldsymbol{r}_i, \dot{\boldsymbol{r}}_i, t) = \sum_i \tfrac{1}{2}\, m_i \dot{\boldsymbol{r}}_i^2 - V(\boldsymbol{r}_i, t), \tag{39}$$

giving Newton's equations.

The Euler-Lagrange equations lead usually to second order differential equations. With the introduction of the canonical momentum for each degree of freedom,

$$p_\alpha \equiv \frac{\partial L}{\partial \dot{q}_\alpha}, \tag{40}$$

one can rewrite the Euler-Lagrange equations as

$$\dot{p}_\alpha = \frac{\partial L}{\partial q_\alpha}, \tag{41}$$

which is a first order differential equation for p_α.

3.2 Hamilton equations

The action principle also allows for the identification of quantities that are conserved in time, two examples of which where already mentioned in our first chapter. Consider the effect of changes of coordinates and time. Since the coordinates are themselves functions of time, we write

$$t \quad \longrightarrow \quad t' = t + \delta t, \tag{42}$$

$$q_\alpha(t) \quad \longrightarrow \quad q'_\alpha(t) = q_\alpha(t) + \delta q_\alpha, \tag{43}$$

and the full variation

$$q_\alpha(t) \;\longrightarrow\; q'_\alpha(t') = q_\alpha(t) + \underbrace{\delta q_\alpha + \dot{q}_\alpha(t)\,\delta t}_{\Delta q_\alpha(t)}. \tag{44}$$

The Euler-Lagrange equations remain valid (obtained by considering any variation), but considering the effect on the surface term, we get in terms of Δq_α and δt the surface term

$$\delta S = \ldots + \left(\sum_\alpha p_\alpha \, \Delta q_\alpha - H \, \delta t \right) \Bigg|_{t_1}^{t_2}, \tag{45}$$

where the quantity H is known as the Hamiltonian

$$H(q_\alpha, p_\alpha, t) = \sum_\alpha p_\alpha \dot{q}_\alpha - L(q_\alpha, \dot{q}_\alpha, t). \tag{46}$$

The full variation of this quantity is

$$\delta H = \sum_\alpha \dot{q}_\alpha \delta p_\alpha - \dot{p}_\alpha \delta q_\alpha - \frac{\partial L}{\partial t}\, \delta t,$$

which shows that it is conserved if L does not explicitly depend on time, while one furthermore can work with q and p as the independent variables (the dependence on $\delta\dot{q}$ drops out). One thus finds the *Hamilton equations*,

$$\dot{q}_\alpha = \frac{\partial H}{\partial p_\alpha} \quad \text{and} \quad \dot{p}_\alpha = -\frac{\partial H}{\partial q_\alpha} \quad \text{with} \quad \frac{dH}{dt} = \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}. \tag{47}$$

The (q, p) space defines the phase space for the classical problem.

For the unconstrained system, we find $\boldsymbol{p}_i = m\,\dot{\boldsymbol{r}}_i$ and

$$H(\boldsymbol{p}_i, \boldsymbol{r}_i, t) = \sum_i \frac{\boldsymbol{p}_i^2}{2m_i} + V(\boldsymbol{r}_i, t), \tag{48}$$

and

$$\dot{\boldsymbol{r}}_i = \frac{\boldsymbol{p}_i}{m_i} \quad \text{and} \quad \dot{\boldsymbol{p}}_i = -\frac{\partial V}{\partial \boldsymbol{r}_i} \quad \text{with} \quad \frac{dH}{dt} = \frac{\partial V}{\partial t}. \tag{49}$$

3.3 Conserved quantities (Noether's theorem)

Next we generalize the transformations to any continuous transformation. In general, one needs to realize that a transformation may also imply a change of the Lagrangian,

$$L(q_\alpha, \dot{q}_\alpha, t) \to L(q_\alpha, \dot{q}_\alpha, t) + \frac{d\Lambda(q_\alpha, \dot{q}_\alpha, t)}{dt}, \tag{50}$$

that doesn't affect the Euler-Lagrange equations, because it changes the action with a boundary term,

$$S(t_1, t_2) \to S(t_1, t_2) + \Lambda(q_\alpha, \dot{q}_\alpha, t)\Big|_{t_1}^{t_2}. \tag{51}$$

Let λ be the continuous parameter (e.g. time shift τ, translation a_x, rotation angle ϕ, ...), then $\Delta q_\alpha = (dq'_\alpha/d\lambda)_{\lambda=0}\,\delta\lambda$, $\delta t = (dt'/d\lambda)_{\lambda=0}\,\delta\lambda$, and $\Delta\Lambda = (d\Lambda/d\lambda)_{\lambda=0}\,\delta\lambda$. This gives rise to a surface term of the form $(Q(t_2) - Q(t_1))\delta\lambda$, or a conserved quantity

$$Q(q_\alpha, p_\alpha, t) = \sum_\alpha p_\alpha \left(\frac{dq'_\alpha}{d\lambda}\right)_{\lambda=0} + H\left(\frac{dt'}{d\lambda}\right)_{\lambda=0} - \left(\frac{d\Lambda}{d\lambda}\right)_{\lambda=0}. \tag{52}$$

==========

Exercise: Get the conserved quantities for time translation ($t' = t + \tau$ and $\boldsymbol{r}' = \boldsymbol{r}$) for a one-particle system with $V(\boldsymbol{r}, t) = V(\boldsymbol{r})$.

==========

Exercise: Get the conserved quantity for space translations ($t' = t$ and $\boldsymbol{r}' = \boldsymbol{r} + \boldsymbol{a}$) for a system of two particles with a potential of the form $V(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = V(\boldsymbol{r}_1 - \boldsymbol{r}_2)$.

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Exercise: Show for a one-particle system with potential $V(\boldsymbol{r}, t) = V(|\boldsymbol{r}|)$ that for rotations around the z-axis (coordinates that change are $x' = \cos(\alpha)\,x - \sin(\alpha)\,y$ and $y' = \sin(\alpha)\,x + \cos(\alpha)\,y$) the conserved quantity is $\ell_z = xp_y - yp_z$.

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Exercise: Consider the special Galilean transformation or boosts in one dimension. The change of coordinates corresponds to looking at the system from a moving frame with velocity u. Thus $t' = t$ and $x' = x - ut$. Get the conserved quantity for a one-particle system with $V(x, t) = 0$.

==========

Exercise: Show that in the situation that the Lagrangian is not invariant but changes according to

$$L' = L + \frac{d\Lambda}{dt} + \Delta L_{SB}$$

(that means a change that is 'more' than just a full time derivative, referred to as the symmetry breaking part ΔL_{SB}), one does not have a conserved quantity. One finds

$$\frac{dQ}{dt} = \left(\frac{d\,\Delta L_{SB}}{d\lambda}\right)_{\lambda=0}.$$

Apply this to the previous exercises by relaxing the conditions on the potential.

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3.4 Poisson brackets

If we have an quantity $A(q_i, p_i, t)$ depending on (generalized) coordinates q and the canonical momenta p_i and possible explicit time-dependence, we can write

$$\begin{aligned} \frac{dA}{dt} &= \sum_i \left(\frac{\partial A}{\partial q_i}\,\dot{q}_i + \frac{\partial A}{\partial p_i}\,\dot{p}_i \right) + \frac{\partial A}{\partial t} \\ &= \sum_i \left(\frac{\partial A}{\partial q_i}\,\frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i}\,\frac{\partial H}{\partial q_i} \right) + \frac{\partial A}{\partial t} = \{A, H\}_{\scriptscriptstyle P} + \frac{\partial A}{\partial t}. \end{aligned} \tag{53}$$

The quantity

$$\{A, B\}_{\scriptscriptstyle P} \equiv \sum_i \left(\frac{\partial A}{\partial q_i}\,\frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i}\,\frac{\partial B}{\partial q_i} \right) \tag{54}$$

is the *Poisson bracket* of the quantities A and B. It is a bilinear product which has the following properties (omitting subscript P),

(1) $\{A, A\} = 0 \quad \text{or} \quad \{A, B\} = -\{B, A\}$,
(2) $\{A, BC\} = \{A, B\}C + B\{A, C\}$ (Leibniz identity),
(3) $\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, G\}\}$ (Jacobi identity).

You may remember these properties for commutators of two operators $[A, B]$ in linear algebra or quantum mechanics. One has the basic brackets,

$$\{q_i, q_j\}_{\scriptscriptstyle P} = \{p_i, p_j\}_{\scriptscriptstyle P} = 0 \quad \text{and} \quad \{q_i, p_j\}_{\scriptscriptstyle P} = \delta_{ij}. \tag{55}$$

Many of our previous relations may now be written with the help of Poisson brackets, such as

$$\dot{q}_i = \{q_i, H\}_{\scriptscriptstyle P} \quad \text{and} \quad \dot{p}_i = \{p_i, H\}_{\scriptscriptstyle P}. \tag{56}$$

Furthermore making a *canonical transformation* in phase space, going from $(q, p) \to (\tilde{q}, \tilde{p})$ such that $\{\tilde{q}(q,p), \tilde{p}(q,p)\} = 1$, one finds that for $A(p, q) = \tilde{A}(\tilde{p}, \tilde{q})$ the Poisson brackets $\{A(p,q), B(p,q)\}_{qp} = \{\tilde{A}(\tilde{p}, \tilde{q}), \tilde{B}(\tilde{p}, \tilde{q})\}_{\tilde{q}\tilde{p}}$, i.e. they remain the same taken with respect to (q, p) or $(\tilde{q}, \tilde{p})$.

A particular set of canonical transformations, among them very important space-time transformations such as translations and rotations, are those of the type

$$q_i' = q_i + \delta q_i = q_i + \frac{\partial G}{\partial p_i}\,\delta\lambda, \tag{57}$$

$$p_i' = p_i + \delta p_i = p_i - \frac{\partial G}{\partial q_i}\delta\lambda. \tag{58}$$

This implies that

$$\delta A(p_i, q_i) = \sum_i \left(\frac{\partial A}{\partial q_i}\,\delta q_i + \frac{\partial A}{\partial p_i}\,\delta p_i \right) = \sum_i \left(\frac{\partial A}{\partial q_i}\,\frac{\partial G}{\partial p_i} + \frac{\partial A}{\partial p_i}\,\frac{\partial G}{\partial q_i} \right) \delta\lambda = \{A, G\}_{\scriptscriptstyle P}\delta\lambda \tag{59}$$

Quantities G of this type are called *generators* of symmetries. For the Hamiltonian (omitting explicit time dependence) one has $\delta H(p_i, q_i) = \{H, G\}_{\scriptscriptstyle P}\delta\lambda$. Looking at the constants of motion Q in Eq. 52 one sees that those that do not have explicit time dependence leave the Hamiltonian invariant and have vanishing Poisson brackets $\{H, Q\}_{\scriptscriptstyle P} = 0$. *These constants of motion thus generate the symmetry transformations of the Hamiltonian.*

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Exercise: Study the infinitesimal transformations for time and space translations, rotations and boosts. Show that they are generated by the conserved quantities that you have found in the previous exercises (that means, check the Poisson brackets of the quantities with coordinates and momenta).

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Exercise: Show that the Poisson bracket of the components of the angular momentum vector $\boldsymbol{\ell} = \boldsymbol{r} \times \boldsymbol{p}$ satisfy

$$\{\ell_x, \ell_y\}_P = \ell_z.$$

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4 Symmetries

In this chapter, we want to complete the picture by discussing symmetries in all of their glory, in particular the space-time symmetries, translations, rotations and boosts. They are important, because they change time, coordinates and momenta, but in such a way that they leave basic quantities invariant (like Lagrangian and/or Hamiltonian) or at least they leave them in essence invariant (up to an irrelevant change that can be expressed as a total time derivative). Furthermore, they modify coordinates and momenta in such a way that these retain their significance as canonical variables. We first consider the full set of (non-relativistic) space-time transformations known as the Galilean group. These include ten transformations, each of them governed by a (real) parameter. They are one time translation, three space translations (one for each direction in space), three rotations (one for each plane in space) and three boosts (one for each direction in space). They change the coordinates

$$t \quad \to \quad t' = t + \tau, \qquad \text{one time translation,} \tag{60}$$

$$\boldsymbol{r} \quad \to \quad \boldsymbol{r}' = \boldsymbol{r} + \boldsymbol{a} \qquad \text{three translations,} \tag{61}$$

$$\boldsymbol{r} \quad \to \quad \boldsymbol{r}' = R(\hat{n}, \alpha)\boldsymbol{r} \qquad \text{three rotations,} \tag{62}$$

$$\boldsymbol{r} \quad \to \quad \boldsymbol{r}' = \boldsymbol{r} - \boldsymbol{u}t \qquad \text{three boosts.} \tag{63}$$

with parameters being (τ, $\boldsymbol{a}$, $\alpha\hat{n}$, $\boldsymbol{u}$). The Lagrangian and Hamiltonian that respect this symmetry are the ones for a free particle or in the case of a many particle system, those for the center of mass system,

$$L = \frac{1}{2}\, m\dot{\boldsymbol{r}}^2 \quad \text{and} \quad H = \frac{\boldsymbol{p}^2}{2m}.$$

with $\boldsymbol{p} = m\dot{\boldsymbol{r}}$.

4.1 Space translations

Let's look at the translations $T(\boldsymbol{a})$ in space. It is clear what is happening with positions and momenta,

$$\boldsymbol{r} \to \boldsymbol{r}' = \boldsymbol{r} + \boldsymbol{a} \quad \text{and} \quad \boldsymbol{p} \to \boldsymbol{p}' = \boldsymbol{p}. \tag{64}$$

and infinitesimally,

$$\delta\boldsymbol{r} = \delta\boldsymbol{a} \quad \text{and} \quad \delta\boldsymbol{p} = 0. \tag{65}$$

This is through Noether's theorem consistent with 'conserved quantities' $\boldsymbol{Q}\cdot\delta\boldsymbol{a} = \boldsymbol{p}\cdot\delta\boldsymbol{a}$, thus the momenta $\boldsymbol{p}$, which also generate the translations (see Eq. 59),

$$\delta x_i = \{x_i, \boldsymbol{p}\}_P\cdot\delta\boldsymbol{a} = \delta a_i \quad \text{and} \quad \delta p_i = -\{p_i, \boldsymbol{p}\}_P\cdot\delta\boldsymbol{a} = 0. \tag{66}$$

Translations in Hilbert space

Let's start with the Hilbert space of functions and look at ways to 'translate a function' and then at ways to 'translate an operator'. Let us work in one dimension. For continuous transformations, it turns out to be extremely useful to look at the infinitesimal problem (in general true for so-called Lie transformations). We get for small a a 'shifted' function

$$\phi'(x) = \phi(x + a) = \phi(x) + a\,\frac{d\phi}{dx} + \ldots = \underbrace{\left(1 + \frac{i}{\hbar}\, a\, p_x + \ldots\right)}_{U(a)}\phi(x), \tag{67}$$

which defines the shift operator $U(a)$ of which the momentum operator $\hat{p}_x = -i\hbar\,(d/dx)$ is referred to as the *generator*. One can extend the above to higher orders,

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

Using the (operator) definition

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

one finds $\phi' = U(a)\phi$ with

$$U(a) = \exp\left(+\frac{i}{\hbar}\,a\,\hat{p}_x\right) = I + \frac{i}{\hbar}\,a\,\hat{p}_x + \ldots\,. \tag{68}$$

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

To see how a translation affects an operator, we look at $O\phi$, which is a function changing as

$$(O\phi)'(x) = O\phi(x+a) = U\,O\phi(x) = \underbrace{U\,O\,U^{-1}}_{O'}\,\underbrace{U\phi}_{\phi'}(x), \tag{69}$$

thus for operators in Hilbert space

$$O \longrightarrow O' = U\,O\,U^{-1} = e^{i\lambda G}\,O\,e^{-i\lambda G}. \tag{70}$$

which expanded gives $O' = (1 + i\lambda G + \ldots)O(1 - i\lambda G + \ldots) = O + i\lambda[G, O] + \ldots$, thus

$$\delta O = -i[O, G]\delta\lambda. \tag{71}$$

One has for the translation operator

$$O' = e^{i\,a\hat{p}_x/\hbar}\,O(0)\,e^{-i\,a\hat{p}_x/\hbar} \quad \text{and} \quad \delta O = -(i/\hbar)\,[O, \hat{p}_x]\,\delta a, \tag{72}$$

which for position and momentum operator gives

$$\delta\hat{x} = -\frac{i}{\hbar}\,[\hat{x}, \hat{p}_x]\,\delta a = \delta a \quad \text{and} \quad \delta\hat{p}_x = -\frac{i}{\hbar}\,[\hat{p}_x, \hat{p}_x]\,\delta a = 0. \tag{73}$$

Note that to show the full transformations for $\hat{x}$ and $\hat{p}_x$ one can use the exact relations

$$i\,\frac{dO'}{d\lambda} = e^{i\,\lambda G}\,\big[O, G\big]\,e^{-i\,\lambda G} \quad \text{and} \quad i\,\frac{dO'}{d\lambda}\bigg|_{\lambda=0} = \big[O, G\big]. \tag{74}$$

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Exercise: Show that for the ket state one has $U(a)|x\rangle = |x - a\rangle$. An *active* translation of a localized state with respect to a fixed frame, thus is given by $|x + a\rangle = U^{-1}(a)|x\rangle = U^\dagger(a)|x\rangle = e^{-i\,ap_x/\hbar}|x\rangle$.

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4.2 Time evolution

Time plays a special role, both in classical mechanics and quantum mechanics. We have seen the central role of the Hamiltonian in classical mechanics (conserved energy) and the dual role as time evolution and energy operator in quantum mechanics. Actively describing time evolution,

$$\psi(t+\tau) = \psi(t) + \tau\,\frac{d\psi}{dt} + \ldots = \underbrace{\left(1 - \frac{i}{\hbar}\,\tau\,H + \ldots\right)}_{U(\tau)}\psi(t), \tag{75}$$

we see that evolution is generated by the Hamiltonian $H = i\hbar\, d/dt$ and given by the (unitary) operator

$$U(\tau) = \exp\left(-i\,\tau\,H/\hbar\right). \tag{76}$$

Since time evolution is usually our aim in solving problems, it is necessary to *know* the Hamiltonian, usually in terms of the positions, momenta (and spins) of the particles involved. If this Hamiltonian is time-independent, we can solve for its eigenfunctions, $H\phi_n(x) = E_n\,\phi_n(x)$ and use completeness to get the general time-dependence (see Eq. 26).

Schrödinger and Heisenberg picture

The time evolution from $t_0 \to t$ of a quantum mechanical system thus is generated by the Hamiltonian,

$$U(t,t_0) = \exp\left(-i(t-t_0)H/\hbar\right), \quad \text{satisfying} \quad i\hbar\,\frac{\partial}{\partial t}U(t,t_0) = H\,U(t,t_0). \tag{77}$$

Two situations can be distinguished:

(i) *Schrödinger picture*, in which the operators are time-independent, $A_S(t) = A_S$ and the states are time dependent, $|\psi_S(t)\rangle = U(t,t_0)|\psi_S(t_0)\rangle$,

$$i\hbar\,\frac{\partial}{\partial t}|\psi_S\rangle \;=\; H\,|\psi_S\rangle, \tag{78}$$

$$i\hbar\,\frac{\partial}{\partial t}A_S \;\equiv\; 0. \tag{79}$$

(ii) *Heisenberg picture*, in which the states are time-independent, $|\psi_H(t)\rangle = |\psi_H\rangle$, and the operators are time-dependent, $A_H(t) = U^{-1}(t,t_0)\,A_H(t_0)\,U(t,t_0)$,

$$i\hbar\,\frac{\partial}{\partial t}|\psi_H\rangle \;\equiv\; 0, \tag{80}$$

$$i\hbar\,\frac{\partial}{\partial t}A_H \;=\; [A_H, H]. \tag{81}$$

We note that in the Heisenberg picture one has the equivalence with classical mechanics, because the time-dependent classical quantities are considered as time-dependent operators. In particular we have

$$i\hbar\,\frac{d}{dt}\hat{\boldsymbol{r}}(t) = [\boldsymbol{r}, H] \quad \text{and} \quad i\hbar\,\frac{d}{dt}\hat{\boldsymbol{p}}(t) = [\boldsymbol{p}, H], \tag{82}$$

to be compared with the classical Hamilton equations.

==========

Exercise: Show that the time dependence of expectation values is the same in the two pictures, i.e.

$$\langle\psi'_S(t)|A_S|\psi_S(t)\rangle = \langle\psi'_H|A_H(t)|\psi_H\rangle.$$

This is important to get the Ehrenfest relations in Eqs 31 and 32 from the Eqs 82.

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4.3 Rotational symmetry

Rotations are characterized by a rotation axis ($\hat{n}$) and an angle ($0 \leq \alpha \leq 2\pi$),

$$\boldsymbol{r} \longrightarrow \boldsymbol{r}' = R(\hat{n}, \alpha)\, \boldsymbol{r} \qquad \text{or} \qquad \varphi \longrightarrow \varphi' = \varphi + \alpha, \tag{83}$$

where the latter refers to the polar angle around the $\hat{n}$-direction. The rotation $R(\hat{z}, \alpha)$ around the z-axis is given by

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \longrightarrow \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{84}$$

==========

Exercise: Check that for polar coordinates (defined with respect to the z-axis),

$$x = r\, \sin\theta\, \cos\varphi, \quad y = r\, \sin\theta\, \sin\varphi, \quad z = r\, \cos\theta,$$

the rotations around the z-axis only change the azimuthal angle, $\varphi' = \varphi + \alpha$.

==========

Conserved quantities and generators in classical mechanics

Using Noether's theorem, we construct the conserved quantity for a rotation around the z-axis. One has the infinitesimal changes $\delta x = -y\,\delta\alpha$ and $\delta y = x\,\delta\alpha$, thus $Q_z \delta\alpha = p_x \delta x + p_y \delta y + p_z \delta z = (x p_y - y p_x)\delta\alpha$, thus $Q_z = \ell_z$ and in general for all rotations all components of the angular momentum $\boldsymbol{\ell}$ are conserved, at least if $\{H, \boldsymbol{\ell}\}_P = 0$. The angular momenta indeed generate the symmetry, leading to

$$\delta x = \{x, \ell_z\}_P \delta\alpha = -y\delta\alpha \quad \text{and} \quad \delta y = \{y, \ell_z\}_P \delta\alpha = x\delta\alpha, \tag{85}$$

$$\delta p_x = \{p_x, \ell_z\}_P \delta\alpha = -p_y\delta\alpha \quad \text{and} \quad \delta p_y = \{p_y, \ell_z\}_P \delta\alpha = p_x\delta\alpha. \tag{86}$$

with as general expressions for the Poisson brackets

$$\{\ell_i, x_j\}_P = \epsilon_{ijk}\, x_k \quad \text{and} \quad \{\ell_i, p_j\}_P = \epsilon_{ijk}\, p_k. \tag{87}$$

The result found for the $\{\ell_i, \ell_j\}_P = \epsilon_{ijk}\, \ell_k$ bracket indicates that angular momenta also change like vectors under rotations.

Rotation operators in Hilbert space

Rotations also gives rise to transformations in the Hilbert space of wave functions. Using polar coordinates and a rotation around the z-axis, we find

$$\phi(r, \theta, \varphi + \alpha) = \phi(r, \theta, \varphi) + \alpha\, \frac{\partial}{\partial\varphi}\, \phi + \ldots = \underbrace{\left(1 + \frac{i}{\hbar}\, \alpha\, \ell_z + \ldots\right)}_{U(\hat{z}, \alpha)} \phi, \tag{88}$$

from which one concludes that $\ell_z = -i\hbar(\partial/\partial\varphi)$ is the generator of rotations around the z-axis in Hilbert space. As we have seen, in Cartesian coordinates this operator is $\ell_z = -i\hbar(x\,\partial/\partial y - y\,\partial/\partial x) = x p_y - y p_x$, the z-component of the (orbital) angular momentum operator $\boldsymbol{\ell} = \boldsymbol{r} \times \boldsymbol{p}$.

The full rotation operator in the Hilbert space is

$$U(\hat{z}, \alpha) = \exp\left(+\frac{i}{\hbar}\, \alpha\, \ell_z\right) = 1 + \frac{i}{\hbar}\, \alpha\, \ell_z + \ldots\ . \tag{89}$$

The behavior of the various quantum operators under rotations is given by

$$O' = e^{i\alpha\ell_z/\hbar}\, O\, e^{-i\alpha\ell_z/\hbar} \quad \text{or} \quad \delta O = -\frac{i}{\hbar}[O, \ell_z]\, \delta\alpha. \tag{90}$$

Using the various commutators calculated for quantum operators in Hilbert space (starting from the basic $[x_i, p_j] = i\hbar\, \delta_i j$ commutator,

$$[\ell_i, r_j] = i\hbar\, \epsilon_{ijk}\, r_k, \quad [\ell_i, p_j] = i\hbar\, \epsilon_{ijk}\, p_k, \quad \text{and} \quad [\ell_i, \ell_j] = i\hbar\, \epsilon_{ijk}\, \ell_k, \tag{91}$$

(note again their full equivalence with Poisson brackets) one sees that the behavior under rotations of the quantum operators $\boldsymbol{r}$, $\boldsymbol{p}$ and $\boldsymbol{\ell}$ is identical to that of the classical quantities. This is true infinitesimally, but also for finite rotations one has for operators $\boldsymbol{r} \to \boldsymbol{r}' = R(\hat{n}, \alpha)\boldsymbol{r}$ and $\boldsymbol{p} \to \boldsymbol{p}' = R(\hat{n}, \alpha)\boldsymbol{p}$. Finally the rotational invariance of the Hamiltonian corresponds to $[H, \boldsymbol{\ell}] = 0$ and in that case it also implies time independence of the Heisenberg operator or the the expectation values $\langle\boldsymbol{\ell}\rangle$.

Generators of rotations in Euclidean space

A characteristic difference between rotations and translations is the importance of the order. The order in which two consecutive translations are performed does not matter $T(\boldsymbol{a})\, T(\boldsymbol{b}) = T(\boldsymbol{b})\, T(\boldsymbol{a})$. This is also true for the Hilbert space operators $U(\boldsymbol{a})\, U(\boldsymbol{b}) = U(\boldsymbol{b})\, U(\boldsymbol{a})$. The order does matter for rotations. This is so in coordinate space as well as Hilbert space, $R(\hat{x}, \alpha)\, R(\hat{y}, \beta) \neq R(\hat{y}, \beta)\, R(\hat{x}, \alpha)$ and $U(\hat{x}, \alpha)\, U(\hat{y}, \beta) \neq U(\hat{y}, \beta)\, U(\hat{x}, \alpha)$.

Going back to Euclidean space and looking at the infinitesimal form of rotations around the z-axis,

$$R(\hat{\boldsymbol{z}}, \delta\alpha) = 1 - i\ \delta\alpha\ J_z \tag{92}$$

one also can identify here the generator

$$J_z = \frac{1}{-i}\ \frac{\partial R(\alpha, \hat{\boldsymbol{z}})}{\partial\varphi}\bigg|_{\alpha=0} = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{93}$$

In the same way we can consider rotations around the x- and y-axes that are generated by

$$J_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \qquad J_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}, \tag{94}$$

The generators in Euclidean space do not commute. Rather they satisfy

$$[J_i, J_j] = i\, \epsilon_{ijk}\, J_k. \tag{95}$$

The same non-commutativity of generators is exhibited in Hilbert space by the commutator of the corresponding quantum operators $\hat{\boldsymbol{\ell}}/\hbar$ and by the Poisson brackets for the conserved quantities in classical mechanics. But realize an important point. Although identical, the commutation relations for $\hat{\boldsymbol{\ell}}$ are in Hilbert space, found starting from the basic (canonical) commutation relations between $\boldsymbol{r}$ and $\boldsymbol{p}$ operators! The consistence of commutation relations in Hilbert space with the requirements of symmetries is a prerequisite for achieving a consistent quantization of theories.

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Exercise: For rotation operations, we have seen that the commutation relations for differential operators $\boldsymbol{\ell}/\hbar$ and for Euclidean rotation matrices $\boldsymbol{J}$ are identical. It is also possible to get a representation in a matrix space for the translations. Embedding the three-dimensional space in a 4-dimensional one, $(x, y, z) \to (x, y, z, 1)$, the rotations and translations can be described by

$$R_z(\alpha) = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 & 0 \\ \sin\alpha & \cos\alpha & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \qquad T(\boldsymbol{a}) = \begin{pmatrix} 1 & 0 & 0 & a_x \\ 0 & 1 & 0 & a_y \\ 0 & 0 & 1 & a_z \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

Check this and find the generators J_z, P_x, P_y and P_z. The latter are found as $T(\delta\boldsymbol{a}) = 1 + i\,\delta\boldsymbol{a}\cdot\boldsymbol{P}$. Calculate the commutation relations between the generators in this (extended) Euclidean space. You will find

$$[J_i, P_j] = i\,\epsilon_{ijk} P_k \tag{96}$$

(at least for $i = 3$ using J_z). Compare these relations with those for the (quantum mechanical) differential operators and the classical Poisson brackets.

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4.4 Boost invariance

For the free particle lagrangian, we consider the boost transformation (going to a frame moving with velocity $\boldsymbol{u}$), governed by real parameters $\boldsymbol{u}$,

$$t' = t \quad \text{and} \quad \boldsymbol{r}' = \boldsymbol{r} - \boldsymbol{u}\,t, \quad \text{and} \quad \boldsymbol{p}' = \boldsymbol{p} - m\,\boldsymbol{u}. \tag{97}$$

while also the Lagrangian and Hamiltonian change but with a total derivative,

$$L' = L + \frac{d}{dt}\underbrace{\left(m\,\boldsymbol{r}\cdot\boldsymbol{u} + \tfrac{1}{2}\,m\,\boldsymbol{u}^2\,t\right)}_{\Lambda}. \tag{98}$$

The (classical) conserved quantities from Noether's theorem become

$$\boldsymbol{K} = t\,\boldsymbol{p} - m\,\boldsymbol{r}. \tag{99}$$

which is conserved because one has

$$\{\boldsymbol{K}, H\}_P = \boldsymbol{p} \quad \text{and} \quad \frac{\partial \boldsymbol{K}}{\partial t} = \boldsymbol{p}, \quad \text{thus} \quad \frac{d\boldsymbol{K}}{dt} = 0. \tag{100}$$

The nature of $\boldsymbol{K}$ is seen in

$$\{K_i, K_j\}_P = 0, \quad \{\ell_i, K_j\}_P = \epsilon_{ijk}\,K_k. \tag{101}$$

The way it changes the coordinates, momenta is consistent with

$$\{K_i, r_j\}_P = -t\,\delta_{ij}, \quad \{K_i, p_j\}_P = m\,\delta_{ij}. \tag{102}$$

In the Hilbert space of quantum operators the basic commutator $[r_i, p_j] = i\hbar\,\delta_{ij}$ is sufficient to reproduce all the above Poisson brackets as commutators in Hilbert space, where the boost operator is given by

$$U(\boldsymbol{u}) = \exp i\boldsymbol{u}\cdot\boldsymbol{K}/\hbar. \tag{103}$$

Explicitly we have for the quantum operators

$$]\boldsymbol{K}, H] = i\hbar \boldsymbol{p} \quad \text{and} \quad \frac{\partial \boldsymbol{K}}{\partial t} = \boldsymbol{p}, \quad \text{thus} \quad \frac{d\langle \boldsymbol{K} \rangle}{dt} = 0, \tag{104}$$

$$[K_i, K_j] = 0, \quad [\ell_i, K_j] = i\hbar \epsilon_{ijk} K_k. \tag{105}$$

$$[K_i, r_j] = -i\hbar t\, \delta_{ij}, \quad [K_i, p_j] = i\hbar m\, \delta_{ij}. \tag{106}$$

Finally if one implements the transformations in space-time, e.g. writing them as matrices as done for rotations and translations, one gets a set of ten generators of the Gallilei transformations, which are denoted as H (time translation generator), $\boldsymbol{P}$ (three generators of translations), $\boldsymbol{J}$ (three generators of rotations) and $\boldsymbol{K}$ (three generators for boosts). They satisfy

$$\begin{aligned} &[P_i, P_j] = [P_i, H] = [J_i, H] = 0, \\ &[J_i, J_j] = i\,\epsilon_{ijk} J_k, \quad [J_i, P_j] = i\,\epsilon_{ijk} P_k, \quad [J_i, K_j] = i\,\epsilon_{ijk} K_k, \\ &[K_i, H] = i\,P_i, \quad [K_i, K_j] = 0, \quad [K_i, P_j] = i\,m\,\delta_{ij}. \end{aligned} \tag{107}$$

This structure is indeed realized in the description of the quantum world. The commutator structure of the symmetry group (Lie algebra of generators) is the same as the commutator structure in the Hilbert space or the Poisson bracket structure in the phase space of classical mechanics. To be precise

$$i\{u, v\}_P \iff \frac{[\hat{u}, \hat{v}]}{\hbar}. \tag{108}$$

are homomorphic to the commutation relations of the generators in the symmetry group, while the correspondence between Poisson brackets and quantum commutation relations is further extended to coordinates and momenta.

4.5 The two-particle system

We ended the previous section with the commutation relations that should be valid for a free-moving system to which the invariance under Gallilei transformations applies. It is easy to check that for a single (free) particle the classically conserved quantities and the quantum mechanical set of operators

$$H = mc^2 + \frac{\boldsymbol{p}^2}{2m}, \tag{109}$$

$$\boldsymbol{P} = \boldsymbol{p}, \tag{110}$$

$$\boldsymbol{J} = \boldsymbol{\ell} + \boldsymbol{s} = \boldsymbol{r} \times \boldsymbol{p} + \boldsymbol{s} \tag{111}$$

$$\boldsymbol{K} = m\boldsymbol{r} - t\boldsymbol{p}. \tag{112}$$

satisfy the required Poisson brackets in classical phase space and the required commutation relations in Hilbert space, in the latter case starting with the canonical commutation relations $[r_i, p_j] = i\hbar\,\delta_{ij}$. This is true even if we allow for a set of spin operators $[s_i, s_j] = i\hbar\,\epsilon_{ijk}\,s_k$ as long as these satisfy $[r_i, s_j] = [p_i, s_j] = 0$. The latter two commutators imply that spin decouples from the spatial part of the wave function. In classical language one would phrase this as that the spins do not depend on position or velocity/momentum. A constant contribution to the energy doesn't matter either. Upon adding a potential $V(\boldsymbol{r})$ to the Hamiltonian, the symmetry requirements would fail and we do not have Gallilei invariance. A potential (e.g. centered around an origin) breaks translation invariance, the specific $\boldsymbol{r}$-dependence might break rotational invariance, etc.

As we have seen, for two particles it is convenient to change to CM and relative coordinates $\boldsymbol{R}$ and $\boldsymbol{r}$ with dorresponding conjugate momenta $\boldsymbol{P}$ and $\boldsymbol{p}$. and introduce the sum mass M and the reduced mass m. The center of mass system should reflect again a free particle. On the other hand, the behavior

under Gallilei transformations, implies applying the transformation to both coordinates. The sum of the generators is given by

$$\begin{aligned} H &= H_1 + H_2 = \frac{\boldsymbol{P}^2}{2M} + H_{\rm int}, \\ \boldsymbol{P} &= \boldsymbol{p}_1 + \boldsymbol{p}_2, \\ \boldsymbol{J} &= \boldsymbol{J}_1 + \boldsymbol{J}_2 = \boldsymbol{\ell}_1 + \boldsymbol{s}_1 + \boldsymbol{\ell}_2 + \boldsymbol{s}_2 = \boldsymbol{R} \times \boldsymbol{P} + \boldsymbol{S}, \\ \boldsymbol{K} &= \boldsymbol{K}_1 + \boldsymbol{K}_2 = M\,\boldsymbol{R} - t\,\boldsymbol{P}, \end{aligned} \tag{113}$$

with

$$\boldsymbol{S} = \boldsymbol{r} \times \boldsymbol{p} + \boldsymbol{s}_1 + \boldsymbol{s}_2, \tag{114}$$

$$H_{int} = Mc^2 + \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r}, \boldsymbol{p}, \boldsymbol{s}_1, \boldsymbol{s}_2), \tag{115}$$

only involving relative coordinates or spins (commuting with CM operators). These center of mass generators then satisfy the classical Poisson brackets or quantum commutation relations for the Gallilei group, starting simply from the canonical relations for each of the particles. The CM system behaves as a free (composite) system with constant energy and momentum and a spin determined by the 'relative' orbital angular momentum and the spins of the constituents. The example also shows that even without spins of the constituents ($s_1 = s_2 = 0$) a composite system has an intrinsic angular momentum showing up as its *spin*.

==========

Exercise: Check that the canonical Poisson brackets or commutation relations for $\boldsymbol{r}_1$ and $\boldsymbol{p}_1$ and those for $\boldsymbol{r}_2$ and $\boldsymbol{p}_2$ imply the canonical commutation relations for $\boldsymbol{R}$ and $\boldsymbol{P}$ as well as for $\boldsymbol{r}$ and $\boldsymbol{p}$.

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4.6 Discrete symmetries

Three important discrete symmetries that we will be discuss are space inversion, time reversal and (complex) conjugation.

Space inversion and Parity

Starting with space inversion operation, we consider its implication for coordinates,

$$\boldsymbol{r} \longrightarrow -\boldsymbol{r} \qquad \text{and} \qquad t \longrightarrow t, \tag{116}$$

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

$$\boldsymbol{p} \longrightarrow -\boldsymbol{p} \qquad \text{and} \qquad \boldsymbol{\ell} \longrightarrow \boldsymbol{\ell}. \tag{117}$$

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

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

$$P\phi(\boldsymbol{r}) \equiv \phi(-\boldsymbol{r}). \tag{118}$$

The function $P\phi$ is a new wave function obtained by the action of the *parity operator* P. It is a hermitian operator (convince yourself). The eigenvalues and eigenfunctions of the parity operator,

$$P\phi_\pi(\boldsymbol{r}) = \pi\,\phi_\pi(\boldsymbol{r}), \tag{119}$$

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.

==========

Exercise: Proof that the eigenvalues of P are $\pi = \pm 1$. Although this looks evident, think carefully about the proof, which requires comparing $P^2\phi$ using Eqs 118 and 119.

==========

The action of parity on the operators is as for any operator in the Hilbert space given by

$$A\phi \longrightarrow PA\phi = \underbrace{PAP^{-1}}_{A'}\underbrace{P\phi}_{\phi'}, \quad \text{thus} \quad A \longrightarrow PAP^{-1}. \tag{120}$$

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

$$\boldsymbol{r} \longrightarrow P\boldsymbol{r}P^{-1} = -\hat{\boldsymbol{r}}, \tag{121}$$
$$\boldsymbol{p} \longrightarrow P\boldsymbol{p}P^{-1} = -\hat{\boldsymbol{p}}, \tag{122}$$
$$\boldsymbol{\ell} \longrightarrow P\boldsymbol{\ell}P^{-1} = +\hat{\boldsymbol{\ell}}, \tag{123}$$
$$H(\boldsymbol{r},\boldsymbol{p}) \longrightarrow PH(\boldsymbol{r},\boldsymbol{p})P^{-1} = H(-\boldsymbol{r},-\boldsymbol{p}). \tag{124}$$

If H is invariant under inversion, one has

$$PHP^{-1} = H \quad \Longleftrightarrow \quad [P,H] = 0. \tag{125}$$

This implies that eigenfunctions of H are also eigenfunctions of P, i.e. they are *even* or *odd*. Although P does not commute with $\boldsymbol{r}$ or $\boldsymbol{p}$ (classical quantities are not invariant), the specific behavior $POP^{-1} = -O$ often also is very useful, e.g. in discussing selection rules. The operators are referred to as P-odd operators.

==========

Exercise: Show that the parity operation leaves $\boldsymbol{\ell}$ invariant and show that the parity operator commutes with $\boldsymbol{\ell}^2$ and $\boldsymbol{\ell}_z$. The eigenfunctions of the latter operators (spherical harmonics) indeed are eigenfunctions of P. What is the parity of the Y_ℓ^m's.

==========

Exercise: Show that for a P-even operator (satisfying $POP^{-1} = +O$ or $[P,O] = PO - OP = 0$) the transition probability

$$\text{Prob}_{\alpha\to\beta} = |\langle\beta|O|\alpha\rangle|^2$$

for parity eigenstates is only nonzero if $\pi_\alpha = \pi_\beta$.
What is the selection rule for a P-odd operator (satisfying $POP^{-1} = -O$ or $\{P,O\} = PO + OP = 0$).

==========

Time reversal

In classical mechanics with second order differential equations, one has for time-independent forces automatically time reversal invariance, i.e. invariance under $t \to -t$ and $\boldsymbol{r} \to \boldsymbol{r}$. There seems an inconsistency with quantum mechanics for the momentum $\boldsymbol{p}$ and energy E. Classically it equals $m\dot{\boldsymbol{r}}$ which changes sign, while $\boldsymbol{\nabla} \to \boldsymbol{\nabla}$. Similarly one has classically $E \to E$, while $H = i\hbar(\partial/\partial t)$ appears to change sign. The problem can be solved by requiring time reversal to be accompagnied by a complex conjugation, in which case one consistently has $\boldsymbol{p} = -i\hbar\boldsymbol{\nabla} \to i\hbar\boldsymbol{\nabla} = -\boldsymbol{p}$ and $H \to H$. Furthermore a stationary state $\psi(t) \sim \exp(-iEt)$ now nicely remains invariant, $\psi^*(-t) = \psi(t)$.

Such a consistent description of the time reversal operator in Hilbert space is straightforward. For unitary operators one has (mathematically) also the anti-linear option, where an anti-linear operator satisfies $T(c_1|\phi_1\rangle + c_2|\phi_2\rangle) = c_1^*\, T|\phi_1\rangle + c_2^*\, T|\phi_2\rangle$. It is easily implemented as

$$T|\phi\rangle = \langle T\phi|, \tag{126}$$

which for matrix elements implies

$$\langle\phi|\psi\rangle = \langle\phi|T^\dagger T|\psi\rangle = \langle T\psi|T\phi\rangle = \langle T\phi|T\psi\rangle^* \tag{127}$$

$$\langle\phi|A|\psi\rangle = \langle\phi|T^\dagger T\, A\, T^\dagger T|\psi\rangle = \langle T\phi|T\, A\, T^\dagger|T\psi\rangle^*. \tag{128}$$

Operators satisfying $TT^\dagger = T^\dagger T = 1$, but swapping bra and ket space (being anti-linear) are known as anti-unitary operators.

Together with conjugation C, which for spinless systems is just complex conjugation, one can look at CPT-invariance by combining the here discussed discrete symmetries. For all known interactions in the world the combined CPT transformation appears to be a good symmetry. The separate discrete symmetries are violated, however, e.g. space inversion is broken by the weak force that causes decays of elementary particles with clear left-right asymmetries. Also T and CP have been found to be broken.

4.7 A relativistic extension*

The symmetry group for relativistic systems is the Poincaré group, with as essential difference that boosts (with parameter $\boldsymbol{u}$ still representing a moving frame, are (for a boost in the x-direction given by

$$ct' = \gamma\, ct - \beta\gamma\, x \tag{129}$$

$$x' = x - \beta\gamma\, ct, \tag{130}$$

while $y' = y$ and $z' = z$. The quantities β and γ are given by

$$\beta = \frac{u}{c} \quad \text{and} \quad \gamma = \frac{1}{\sqrt{1-\beta^2}} = \frac{1}{\sqrt{1-u^2/c^2}}. \tag{131}$$

These transformations guarantee that the velocity of light is constant in any frame, satisfying

$$c^2t^2 - \boldsymbol{r}^2 = c^2t'^2 - \boldsymbol{u}'^2 = c^2\tau^2, \tag{132}$$

where τ is referred to as eigentime (time in rest-frame of system). Mathematically one can look at this structure as we did for rotations and find the commutation relations of the Poincaré group

$$\begin{aligned}
&[P^i, P^j] = [P^i, H] = [J^i, H] = 0,\\
&[J^i, J^j] = i\,\epsilon^{ijk}J^k, \quad [J^i, P^j] = i\,\epsilon^{ijk}P^k, \quad [J^i, K^j] = i\,\epsilon^{ijk}K^k,\\
&[K^i, H] = i\,P^i, \quad [K^i, K^j] = -i\,\epsilon^{ijk}J^k/c^2, \quad [K^i, P^j] = i\,\delta^{ij}H/c^2.
\end{aligned} \tag{133}$$

The action of a relativistic free particle is actually extremely simple,

$$S = mc^2 \int d\tau = mc^2 \int dt \ \sqrt{1 - \boldsymbol{v}^2/c^2}. \tag{134}$$

One can find the Lagrangian and Hamiltonian,

$$L = mc^2 \sqrt{1 - \boldsymbol{v}^2/c^2} \quad \text{and} \quad H = \sqrt{m^2 c^4 + \boldsymbol{p}^2 c^2}, \tag{135}$$

where we have $\boldsymbol{p} = m\boldsymbol{v}\,\gamma$. Note that for $E = mc^2\, dt/d\tau$ and $\boldsymbol{p} = mc\, d\boldsymbol{r}/d\tau$, so $(E/c, \boldsymbol{p})$ transform among themselves exactly as $(ct, \boldsymbol{r})$.

For a single free particle or for the CM coordinates, the classically conserved quantities or generators of the Poincaré group can be found using Noether's theorem. They are

$$\begin{aligned} H &= \sqrt{\boldsymbol{p}^2\, c^2 + m^2\, c^4}, \\ \boldsymbol{P} &= \boldsymbol{p}, \\ \boldsymbol{J} &= \boldsymbol{r} \times \boldsymbol{p} + \boldsymbol{s}, \\ \boldsymbol{K} &= \frac{1}{2c^2}\,(\boldsymbol{r}H + H\boldsymbol{r}) - t\boldsymbol{p} + \frac{\boldsymbol{p} \times \boldsymbol{s}}{H + mc^2}. \end{aligned} \tag{136}$$

A consistent relativistic quantum mechanical treatment in terms of relative coordinates, however, requires great care [See e.g. L.L. Foldy, Phys. Rev. 122 (1961) 275 and H. Osborn, Phys. Rev. 176 (1968) 1514] and is possible in an expansion in $1/c$. Interaction terms, however, enter not only in the Hamiltonian, but also in the boost operators.

5 Employing symmetries

5.1 Translation symmetry

Translations are generated by the momentum operator. We have seen how the translation operators act on wave functions, states or operators. We have seen there the use of the commutator in the infinitesimal transformation of operators. The emergence of the commutator can also be seen directly in function space. Look at a Hamiltonian H, that is invariant under translations. This implies that $H(x) = H(x+a)$. What does this imply? Just compare the Taylor expansion of the operator in a with the infinitesimal expansion discussed previously,

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

and we conclude that translation invariance implies

$$H(x+a) = H(x) \iff [p_x, H] = 0. \tag{137}$$

==========

Exercise: show directly (by acting on a wave function) that indeed $-i\hbar(dH/dx) = [p_x, H]$, i.e. show that

$$\big[p_x, H\big]\phi(x) = -i\hbar\left(\frac{dH}{dx}\right)\phi(x).$$

==========

Translation invariance can easily be generalized to translations $T(\boldsymbol{a})$ in three dimensions including also more particles by considering

$$\boldsymbol{r}_i \longrightarrow \boldsymbol{r}_i' = \boldsymbol{r}_i + \boldsymbol{a}. \tag{138}$$

The index i refers to the particular particle. The global quantum mechanical shift operator is

$$U(\boldsymbol{a}) = \exp\left(+\boldsymbol{a}\cdot\sum_i \boldsymbol{\nabla}_i\right) = \exp\left(+\frac{i}{\hbar}\,\boldsymbol{a}\cdot\sum_i \boldsymbol{p}_i\right) = \exp\left(+\frac{i}{\hbar}\,\boldsymbol{a}\cdot\boldsymbol{P}\right), \tag{139}$$

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

Translation invariance of the whole world implies that for $U(\boldsymbol{a})$ in Eq. 139

$$U(\boldsymbol{a})\, H\, U^{-1}(\boldsymbol{a}) = H \iff [\boldsymbol{P}, H] = 0. \tag{140}$$

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.

The eigenfunctions of translation operators

We already have seen these in various forms, formal as momentum states $|\boldsymbol{p}\rangle$, and in function space as $\phi_p(x) = \exp(i\boldsymbol{k}\cdot\boldsymbol{r})$ where $\boldsymbol{p} = \hbar\boldsymbol{k}$. Since the three translation operators commute among themselves, they can be looked at independently and indeed the eigenfunctions in three dimensions is the product of eigenfunctions in one dimension. In the section on coordinate and momentum representation the implications of the normalization for the 'counting' of states (integration in p-space) have been discussed. Using

either coordinate or momentum representation (using the wave number $\boldsymbol{k}$ rather than the momentum $\boldsymbol{p}$ to avoids $\hbar$'s and using $\rho = 1$) we have

$$\psi(\boldsymbol{r}) = \langle \boldsymbol{r}|\psi\rangle = \int \frac{d^3\boldsymbol{k}}{(2\pi)^3}\ \langle \boldsymbol{r}|\boldsymbol{k}\rangle\langle \boldsymbol{k}|\psi\rangle = \int \frac{d^3\boldsymbol{k}}{(2\pi)^3}\ \exp\left(i\,\boldsymbol{k}\cdot\boldsymbol{r}\right)\tilde{\psi}(\boldsymbol{k}), \tag{141}$$

$$\tilde{\psi}(\boldsymbol{k}) = \langle \boldsymbol{k}|\psi\rangle = \int d^3\boldsymbol{r}\ \langle \boldsymbol{k}|\boldsymbol{r}\rangle\langle \boldsymbol{r}|\psi\rangle = \int d^3\boldsymbol{r}\ \exp\left(-i\,\boldsymbol{k}\cdot\boldsymbol{r}\right)\psi(\boldsymbol{r}), \tag{142}$$

mathematically corresponding to Fourier transforming. Actually, Eq. 141 is just the expansion of any wave function in momentum eigenstates using the proper counting (Eq. **??**), while Eq. 142 is just the calculation of the coefficients in this expansion.

In a box, plane waves can actually be normalized, but in that case one also has to impose boundary conditions. Physically, one usually considers the box as the limit of a potential well with infinite walls. Mathematically, the necessity of boundary conditions also follows from the necessity to have a hermitean operator. The boundary condition must guarantee that $-i\hbar\, d/dx$ works to left and right with the same result. Without boundary conditions one also would have an overcomplete set of functions in the box.

Bloch theorem

The Bloch theorem is a very nice application of translation symmetry in solid state physics. We will proof the Bloch theorem in one dimension. Consider a periodic potential (in one dimension), $V(x+d) = V(x)$. One has a periodic Hamiltonian that commutes with the (unitary) shift operator $U(d) = \exp(+i\,d\,p_x/\hbar)$,

$$[H, U(d)] = 0 \tag{143}$$

==========

Exercise: Prove that the Hamiltonian commutes with the translation operator $U(d)$, $[H, U(d)] = 0$ for a periodic potential.

==========

Thus these operators have a common set of eigenstates $\phi_{E,k}$, satisfying $H\,\phi_{E,k}(x) = E\,\phi_{E,k}(x)$ and $U(d)\,\phi_{E,k}(x) = e^{i\,kd}\,\phi_{E,k}(x)$. The latter eigenvalue is written in exponential form. Since a unitary operator doesn't change the normalization, kd is then real and periodic modulo 2π, limited to (for instance) $-\pi \le kd \le \pi$. Using that $U(d)$ is the translation operator, one has

$$\phi_{E,k}(x+d) = e^{i\,kd}\,\phi_{E,k}(x) \tag{144}$$

Equivalently one can write ϕ as a *Bloch wave*

$$\phi_{E,k}(x) \equiv e^{ikx}\,u_{E,k}(x), \tag{145}$$

in which the 'momentum' k is limited to one cell and one finds that $u_{E,k}(x)$ is periodic, satisfying $u_{E,k}(x+d) = u_{E,k}(x)$.

To appreciate this result, realize that for a constant potential (translation invariance or invariance for any value of d or effectively $d \to 0$)) the Bloch wave is constant and the wave function is a plain wave (with no restrictions on k, $-\infty < k < \infty$ and it now truly is the momentum). The energy becomes $E(k) = \hbar^2\,k^2/2m$. For periodic potentials the k-values are limited (Brillouin zone) and the dispersion $E(k)$ exhibits typically a band structure, which can e.g. be easily demonstrated by working out the solutions for a grid of δ-functions or for a block-potential (Kronig-Penney model).

==========

Exercise: We consider the periodic version of a delta function potential, 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. 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

$$\phi_{E,k}(x) = A\,e^{\kappa x} + B\,e^{-\kappa x} \quad \text{with} \quad E = -\frac{\hbar^2\,\kappa^2}{2m}$$

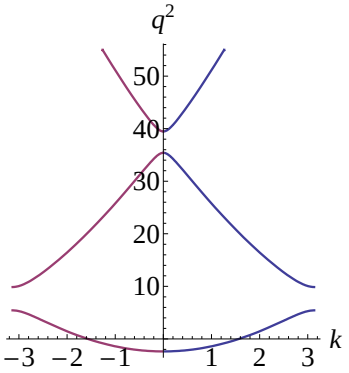
(note: $\kappa = i\,q$).

(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).



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5.2 Rotational symmetry

Eigenfunctions of angular momentum operators

For rotations in a plane, there is only one generator, e.g. the operator $L_z = -i\hbar\partial/\partial\varphi$ for rotations in the x-y plane. Its eigenfunctions are $e^{im\varphi}$ with eigenvalues $m\hbar$ for integer m.

To study the (three) angular momentum operators $\hat{\boldsymbol{\ell}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}} = -i\hbar\, \boldsymbol{r} \times \boldsymbol{\nabla}$, it is useful to use their commutation relations, $[\ell_i, \ell_j] = i\hbar\, \epsilon_{ijk}\, \ell_k$ and the fact that the operator $\boldsymbol{\ell}^2$ commutes with all of them, $[\boldsymbol{\ell}^2, \ell_i] = 0$. To find the explicit form of the functions, it is useful to know the expressions in polar coordinates. Using Eqs **??** and **??**, the $\hat{\boldsymbol{\ell}}$ operators are given by

$$\hat{\ell}_x = -i\hbar \left(y\, \frac{\partial}{\partial z} - z\, \frac{\partial}{\partial y} \right) = i\hbar \left(\sin\varphi\, \frac{\partial}{\partial \theta} + \cot\theta\, \cos\varphi\, \frac{\partial}{\partial \varphi} \right), \tag{146}$$

$$\hat{\ell}_y = -i\hbar \left(z\, \frac{\partial}{\partial x} - x\, \frac{\partial}{\partial z} \right) = i\hbar \left(-\cos\varphi\, \frac{\partial}{\partial \theta} + \cot\theta\, \sin\varphi\, \frac{\partial}{\partial \varphi} \right), \tag{147}$$

$$\hat{\ell}_z = -i\hbar \left(x\, \frac{\partial}{\partial y} - y\, \frac{\partial}{\partial x} \right) = -i\hbar\, \frac{\partial}{\partial \varphi}, \tag{148}$$

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

$$\hat{\ell}^2 = \ell_x^2 + \ell_y^2 + \ell_z^2 = -\hbar^2 \left[\frac{1}{\sin\theta}\, \frac{\partial}{\partial \theta} \left(\sin\theta\, \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta}\, \frac{\partial^2}{\partial \varphi^2} \right]. \tag{149}$$

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 $\hat{\ell}_i(fg) = f\, (\hat{\ell}_i g) + (\hat{\ell}_i f)\, g$.

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 for the eigenfunctions of ℓ_z only the φ dependence matters. The eigenfunctions are of the form $f_m(\varphi) \propto e^{i\, m\varphi}$, 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. In particular, the (simultaneous) eigenfunctions of $\boldsymbol{\ell}^2$ and ℓ_z, referred to as the spherical harmonics, are given by

$$\hat{\ell}^2\, Y_\ell^m(\theta, \varphi) = \ell(\ell + 1)\hbar^2\, Y_\ell^m(\theta, \varphi), \tag{150}$$

$$\hat{\ell}_z\, Y_\ell^m(\theta, \varphi) = m\hbar\, Y_\ell^m(\theta, \varphi), \tag{151}$$

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

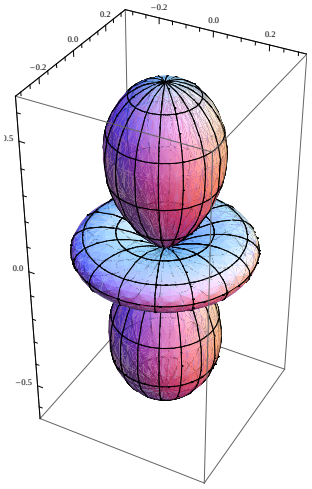
$$Y_0^0(\theta, \varphi) = \frac{1}{\sqrt{4\pi}}. \tag{152}$$

Explicit results for $\ell = 1$ are

$$Y_1^1(\theta, \varphi) = -\sqrt{\frac{3}{8\pi}}\,\frac{x+iy}{r} = -\sqrt{\frac{3}{8\pi}}\,\sin\theta\, e^{i\varphi}, \tag{153}$$

$$Y_1^0(\theta, \varphi) = \sqrt{\frac{3}{4\pi}}\,\frac{z}{r} = \sqrt{\frac{3}{4\pi}}\,\cos\,\theta, \tag{154}$$

$$Y_1^{-1}(\theta, \varphi) = \sqrt{\frac{3}{8\pi}}\,\frac{x-iy}{r} = \sqrt{\frac{3}{8\pi}}\,\sin\theta\, e^{-i\varphi}. \tag{155}$$



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

$$Y_2^{\pm 2}(\theta, \varphi) = \sqrt{\frac{15}{32\pi}}\,\frac{(x^2-y^2) \pm 2i\,xy}{r^2} = \sqrt{\frac{15}{32\pi}}\,\sin^2\theta\, e^{\pm 2i\varphi}, \tag{156}$$

$$Y_2^{\pm 1}(\theta, \varphi) = \mp\sqrt{\frac{15}{8\pi}}\,\frac{z(x \pm iy)}{r^2} = \mp\sqrt{\frac{15}{8\pi}}\,\sin\theta\,\cos\,\theta\, e^{\pm i\varphi}. \tag{157}$$

$$Y_2^0(\theta, \varphi) = \sqrt{\frac{5}{16\pi}}\,\frac{3\,z^2 - r^2}{r^2} = \sqrt{\frac{5}{16\pi}}\,\left(3\cos^2\theta - 1\right), \tag{158}$$

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

$$\int d\Omega\; Y_\ell^{m*}(\theta, \varphi)\, Y_{\ell'}^{m'}(\theta, \varphi) = \delta_{\ell\ell'}\,\delta_{mm'}. \tag{159}$$

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,

$$Y_\ell^m(\theta, \varphi) = (-)^{(m+|m|)/2}\,\sqrt{\frac{2\ell+1}{4\pi}\,\frac{(\ell-|m|)!}{(\ell+|m|)!}}\,P_\ell^{|m|}(\cos\,\theta)\, e^{im\varphi}, \tag{160}$$

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

$$P_\ell^{|m|}(x) = \frac{1}{2^\ell\, \ell!}\,(1-x^2)^{|m|/2}\,\frac{d^{\ell+|m|}}{dx^{\ell+|m|}}\,\left[(x^2-1)^\ell\right]. \tag{161}$$

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

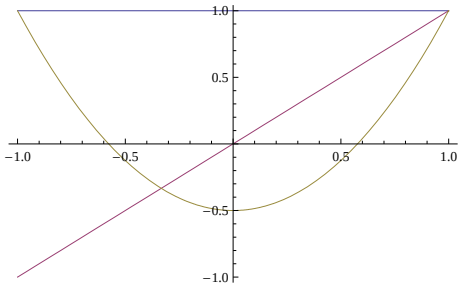
$$P_\ell(\cos\,\theta) = \sqrt{\frac{4\pi}{2\ell+1}}\,Y_\ell^0(\theta). \tag{162}$$

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

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

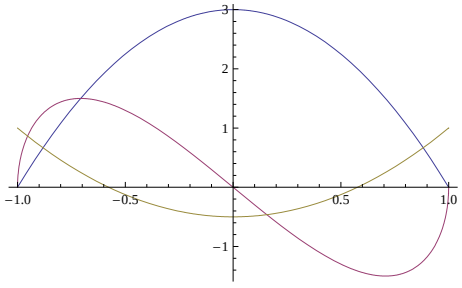
given in the figure to the right.



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

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

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



BCH Relations, etc.

The commutation relations between exponentiated operators is generalized using the linear operations

$$(\mathrm{ad}\,A)B = [A, B], \tag{163}$$

$$(\mathrm{Ad}\,A)B = ABA^{-1}. \tag{164}$$

with $(\mathrm{ad}\,A)^2 B = [A, [A, B]]$, etc. These operations are related through

$$\mathrm{Ad}\,e^A = e^{\mathrm{ad}\,A} \quad \text{or} \quad e^A B e^{-A} = B + [A, B] + \frac{1}{2!}\,[A, [A, B]] + \ldots, \tag{165}$$

which is proven by introducing $F(\tau) = e^{\tau A} B\, e^{-\tau A}$ and showing that $dF/d\tau = (\mathrm{ad}\,A)F$, yielding the result $F(\tau) = e^{\tau\,\mathrm{ad}\,A} B$.

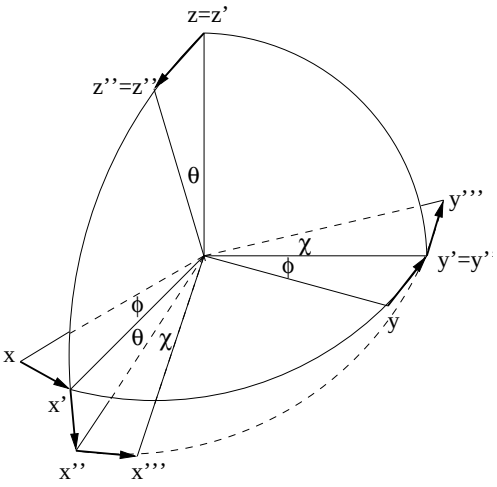
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Exercise: If you like a bit of puzzling, look at the Baker-Campbell-Hausdorff relation

$$e^A\, e^B = e^C \quad \text{with} \quad C = A + B + \frac{1}{2}\,[A, B] + \frac{1}{12}[A, [A, B]] + \frac{1}{12}[B, [A, B]] + \ldots\ ,$$

which shows that (only) for commuting operators one can 'add' operators in the exponent just as numbers.

==========



Euler Rotations

A standard way to rotate any object to a given orientation are the *Euler rotations*. Here one rotates the axes as given in the figure. This corresponds (in our convention) to

$$\begin{aligned} R_E(\varphi,\theta,\chi) &= R(\hat{z}'',-\chi)R(\hat{y}',-\theta)R(\hat{z},-\varphi) \\ &= R(\hat{z},-\varphi)R(\hat{y},-\theta)R(\hat{z},-\chi) \end{aligned}$$

Correspondingly one has the rotation operator in Hilbert space

$$U_E(\varphi,\theta,\chi) = e^{-i\varphi\,\ell_z/\hbar}\, e^{-i\theta\,\ell_y/\hbar}\, e^{-i\chi\,\ell_z/\hbar}. \qquad (166)$$

Using the rotation $U_E(\varphi,\theta,\chi)$ to orient an axi-symmetric object (around z-axis) in the direction $\hat{n}$ with polar angles θ and φ, the angle χ doesn't play a role. In order to get nicer symmetry properties, one uses in that case $U_E(\varphi,\theta,-\varphi)$. For a non-symmetric system (with three different moments of inertia) one needs all angles.

5.3 The radial Schrödinger equation

A very important application of rotational symmetry is its use to reduce a three-dimensional problem to a (simpler) one-dimensional problem. In three dimensions the eigenstates of the Hamiltonian for a particle in a potential are found from

$$H\,\psi(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\boldsymbol{r})\right]\psi(\boldsymbol{r}) = E\,\psi(\boldsymbol{r}). \qquad (167)$$

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

$$\begin{aligned} \boldsymbol{\nabla}^2 &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\,\frac{\partial}{\partial r}\right) + \frac{1}{r^2\,\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\,\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2} \qquad (168) \\ &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\,\frac{\partial}{\partial r}\right) - \frac{\boldsymbol{\ell}^2}{\hbar^2\,r^2}. \qquad (169) \end{aligned}$$

where $\boldsymbol{\ell}$ are the three angular momentum operators. If the potential has no angular dependence, one knows that $[H,\boldsymbol{L}] = 0$ and the eigenfunctions can be written as

$$\psi_{n\ell m}(\boldsymbol{r}) = R_{n\ell m}(r)\,Y_\ell^m(\theta,\varphi). \qquad (170)$$

Inserting this in the eigenvalue equation one obtains

$$\left[-\frac{\hbar^2}{2m\,r^2}\frac{\partial}{\partial r}\left(r^2\,\frac{\partial}{\partial r}\right) + \left(\frac{\hbar^2\,\ell(\ell+1)}{2m\,r^2} + V(r)\right)\right]R_{n\ell}(r) = E_{n\ell}\,R_{n\ell}(r), \qquad (171)$$

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[1].

For the regular solutions, it is convenient to write

$$\psi(\boldsymbol{r}) = R(r)\, Y_\ell^m(\theta,\varphi) = \frac{u(r)}{r}\, Y_\ell^m(\theta,\varphi). \tag{172}$$

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

$$\left[-\frac{\hbar^2}{2m}\,\frac{d^2}{dr^2} + \underbrace{\frac{\hbar^2\,\ell(\ell+1)}{2m\,r^2} + V(r)}_{V_{\rm eff}(r)} - E_{n\ell}\right] u_{n\ell}(r) = 0, \tag{173}$$

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.

==========

Exercise: Show that for an angle-independent operator O

$$\int d^3r\ \psi_1^*(\boldsymbol{r})\, O\, \psi_2(\boldsymbol{r}) = \int_0^\infty r^2\, dr \int d\Omega\ \psi^*_{n'\ell'm'}(\boldsymbol{r})\, O\, \psi_{n\ell m}(\boldsymbol{r}) = \delta_{\ell'\ell}\,\delta_{m'm} \int_0^\infty dr\ u^*_{n'\ell}(r)\, O\, u_{n\ell}(r).$$

==========

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

$$x = \rho\,\cos\varphi, \quad y = \rho\,\sin\varphi, \quad z = z.$$

==========

Exercise: In the previous exercise you have found that the Hamiltonian can be expressed in terms of p_z and ℓ_z, where $p_z = -i\hbar\,\partial/\partial z$ and $\ell_z = -i\hbar\,\partial/\partial\varphi$. Give the most general solution for a cylindrically symmetric potential only depending on ρ, using eigenfunctions of these operators and give the Schrödinger equation that determines the ρ-dependence. Try to simplify this into a truely 'one-dimensional' Schrödinger equation as was done by choosing $R(r) = u(r)/r$ in case of spherical symmetry.

==========

Properties of one-dimensional Schrödinger equations

Using symmetries and defining appropriate degrees of freedom (CM and relative coordinates) one can often reduce a problem to a simpler one, in particular a two-body system can often be reduced to a one-body problem in the CM system and using rotational invariance a one dimensional Schrödinger equation remains.

We recall the nice properties of one dimensional problems:

[1] 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.

- In one dimension any attractive potential has always at least one bound state. This property is only true if one has a one-dimensional domain $-\infty < x < \infty$, so it is not true for the radial Schrödinger equation on the domain $0 \leq r < \infty$.
- 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. Depending on your counting, the radial Schrödinger equation starts with a node because $u(0) = 0$
- Bound state solutions of the one-dimensional Schrödinger equation are nondegenerate. Let's proof this one. Suppose that ϕ_1 and ϕ_2 are two solutions with the same energy. Construct

$$W(\phi_1, \phi_2) = \phi_1(x)\,\frac{d\phi_2}{dx} - \phi_2(x)\,\frac{d\phi_1}{dx}, \tag{174}$$

  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

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

  and hence (when normalized) the functions are identical.

Besides these elementary properties one can often study asymptotic limits, implying oscillatory behavior ($\sin kr$ and $\cos kr$ or complex exponentials $e^{\pm ikr}$) for positive energies $E = \hbar^2 k^2/2m$ or exponential behavior ($e^{\pm\kappa r}$) for negative energies $E = -\hbar^2\kappa^2/2m$. Furthermore one has for a potential that is not more singular at the origin than the angular momentum barrier, the short-distance behavior $u(r) \propto C\,r^{\ell+1}$.

5.4 The spherical solutions for plane waves

The solutions of the Schrödinger equation in the absence of a potential are well-known, namely the plane waves, $\phi_k(\boldsymbol{r}) = \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r})$, characterized by a wave vector $\boldsymbol{k}$ and energy $E = \hbar^2\boldsymbol{k}^2/2m$. But this also represents a spherically symmetric situation, so another systematic way of obtaining the solutions is starting with the radial Schrödinger equation in Eq. 173,

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k^2\right) u_\ell(r) = 0, \tag{175}$$

depending on ℓ. There are two type of solutions of this equation

- Regular solutions: spherical Bessel functions of the first kind: $u_\ell(r) = kr\,j_\ell(kr)$.
  Properties:

$$\begin{aligned} j_0(z) &= \frac{\sin z}{z}, \\ j_\ell(z) &= z^\ell\left(-\frac{1}{z}\,\frac{d}{dz}\right)^\ell \frac{\sin z}{z} \quad \stackrel{z\to 0}{\longrightarrow} \quad z^\ell, \\ & \qquad\qquad\qquad\qquad \stackrel{z\to\infty}{\longrightarrow} \quad \frac{\sin(z-\ell\pi/2)}{z}. \end{aligned}$$

- Irregular solutions: spherical Bessel functions of the second kind: $u_\ell(r) = kr\, n_\ell(kr)$.
  Properties:

$$\begin{aligned} n_0(z) &= -\frac{\cos z}{z}, \\ n_\ell(z) &= -z^\ell \left(-\frac{1}{z}\frac{d}{dz}\right)^\ell \frac{\cos z}{z} \quad \stackrel{z\to 0}{\longrightarrow} \quad z^{-(\ell+1)}, \\ & \qquad\qquad\qquad\qquad \stackrel{z\to\infty}{\longrightarrow} \quad -\frac{\cos(z-\ell\pi/2)}{z}. \end{aligned}$$

Equivalently one can use linear combinations, known as Hankel functions,

$$\begin{aligned} kr\, h_\ell^{(1)}(kr) &= kr\,(j_\ell(kr) + i\, n_\ell(kr)) \quad \stackrel{z\to\infty}{\longrightarrow} \quad (-i)^{\ell+1}\, e^{i\,kr}, \\ kr\, h_\ell^{(2)}(kr) &= kr\,(j_\ell(kr) - i\, n_\ell(kr)) \quad \stackrel{z\to\infty}{\longrightarrow} \quad (i)^{\ell+1}\, e^{-i\,kr}. \end{aligned}$$

Comparing this with the other well-known solution of the free Schrödinger equation in terms of plane waves, it must be possible to express the plane wave as an expansion into these spherical solutions. This expansion is

$$\exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) = e^{i\,kz} = e^{i\,kr\,\cos\theta} = \sum_{\ell=0}^{\infty}(2\ell+1)\, i^\ell\, j_\ell(kr)\, P_\ell(\cos\theta), \tag{176}$$

where the Legendre polynomials P_ℓ as discussed before are related to Y_ℓ^0. Indeed, because of the azimuthal dependence only $m = 0$ spherical harmonics contribute in this expansion.

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Exercise: Compare the (order and pattern of) energies (including degeneracies) of bound states in a cube with those in a sphere.
For this one needs the zeros of the spherical Bessel functions; the first few using $j_\ell(x_{n\ell}) = 0$ are $x_{n0} = n\pi$, $x_{11} = 4.493$, $x_{21} = 7.725$, $x_{12} = 5.763$, $x_{22} = 9.095$, $x_{13} = 6.988$, $x_{14} = 8.183$, $x_{15} = 9.356$.

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5.5 The hydrogen atom (repetition)

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

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \underbrace{\frac{\hbar^2\,\ell(\ell+1)}{2m\,r^2} + V_c(r)}_{V_{\rm eff}(r)} - E\right] u_{n\ell}(r) = 0, \tag{177}$$

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

$$\left[-\frac{d^2}{d\xi^2} + \frac{\ell(\ell+1)}{\xi^2} - \frac{e^2}{4\pi\epsilon_0}\,\frac{2m\,a_0}{\hbar^2}\,\frac{Z}{\xi} - \frac{2m\,a_0^2\,E}{\hbar^2}\right] u_{E\ell}(\xi) = 0. \tag{178}$$

From this dimensionless equation we find that the coefficient multiplying $1/\xi$ 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*

$$a_0 \equiv \frac{4\pi\epsilon_0\,\hbar^2}{m\,e^2}. \tag{179}$$

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

$$R_\infty = \frac{\hbar^2}{2m\,a_0^2} = \frac{1}{2}\,\frac{e^2}{4\pi\epsilon_0\,a_0} = \frac{m\,e^4}{32\pi^2\epsilon_0^2\,\hbar^2}. \tag{180}$$

One then obtains the dimensionless equation

$$\left[-\frac{d^2}{d\xi^2} + \frac{\ell(\ell+1)}{\xi^2} - \frac{2Z}{\xi} - \epsilon\right] u_{\epsilon\ell}(\xi) = 0 \tag{181}$$

with $\xi = r/a_0$ 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,

$$\alpha = \frac{e^2}{4\pi\,\epsilon_0\,\hbar c} \approx 1/137, \tag{182}$$

$$a_0 \equiv \frac{4\pi\epsilon_0\,\hbar^2}{m\,e^2} = \frac{4\pi\epsilon_0\,\hbar c}{e^2}\,\frac{\hbar c}{mc^2} = \frac{1}{\alpha}\,\frac{\hbar c}{mc^2} \approx 0.53\times 10^{-10}\ \text{m}, \tag{183}$$

$$R_\infty = \frac{\hbar^2}{2m\,a_0^2} = \frac{1}{2}\,\alpha\left(\frac{\hbar c}{a_0}\right) = \frac{1}{2}\,\alpha^2\,mc^2 \approx 13.6\ \text{eV}. \tag{184}$$

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! The scaled expressions can also be used to first solve for $Z = 1$ (Hydrogen) and afterwards look at the Hydrogenic case (one electron and nuclear charge Ze). We simply have to realize that one needs the replacements

$$e^2 \;\to\; Z\,e^2 \quad \text{or} \quad \alpha \;\to\; Z\,\alpha, \qquad a_0 \;\to\; a_0/Z, \qquad R_\infty \;\to\; Z^2\,R_\infty. \tag{185}$$

Some aspects of the solution can be easily understood. For instance, looking at equation 181 one sees that the asymptotic behavior of the wave function is found from

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

so one expects for $\xi \to \infty$ the result $u(\xi) \sim e^{-\xi\sqrt{|\epsilon|}} = e^{-\rho}$, with $\rho = \xi\sqrt{|\epsilon|}$. In terms of $E = -\hbar^2\kappa^2/2m$ one has $\rho = \kappa\,r$, showing the expected asymptotic fall-off of the wave function. For $\ell = 0$ one expects for $\rho \to 0$ that $u(\rho) \sim \rho$. Thus it is easy to check that $u_{10}(\rho) \sim \rho\,e^{-\rho}$ is a solution with $\epsilon = -1$.

To find the solutions in general (using $Z = 1$), we can turn to an algebraic manipulation program or a mathematical handbook to look for the solutions of the dimensionless differential equation (see appendix on Laguerre polynomials). It is actually easier to rewrite the equation in terms of ρ (even if it does depend on the specific solution). One gets

$$\left[-\frac{d^2}{d\rho^2} + \frac{\ell(\ell+1)}{\rho^2} - \frac{2/\sqrt{|\epsilon|}}{\rho} - 1\right] u_{\epsilon\ell}(\rho) = 0 \tag{186}$$

and can compare this with a general mathematical treatment of Laguerre polynomials that satisfy this type of differential equation, identifying $2p + a + 1 = 2/\sqrt{|\epsilon|}$, $1 - a^2 = 4\ell(\ell+1)$ and $x = 2\rho$. We then

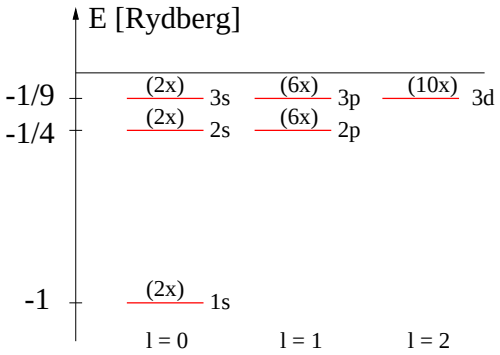
find that $a \to 2\ell+1$ and with $p \to n-\ell-1$ one has $1/\sqrt{|\epsilon|} = n$, The solutions for hydrogen found this way are

$$u_{n\ell}(\xi) = \left(\frac{2}{n\,a_0}\right)^{1/2} \sqrt{\frac{(n-\ell-1)!}{2n\,(n+\ell)!}}\; e^{-\xi/n} \left(\frac{2\xi}{n}\right)^{\ell+1} L^{2\ell+1}_{n-\ell-1}\left(\frac{2\xi}{n}\right) \tag{187}$$

with eigenvalues (energies)

$$E_{n\ell} = -\frac{1}{n^2}\,R_\infty, \tag{188}$$

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 $p = n-\ell-1$ is precisely 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 $\Pi = (-)^\ell$.

Explicitly, the lowest solutions are:

$$u_{10}(r) = 2\left(\frac{1}{a_0}\right)^{1/2} e^{-r/a_0}\left(\frac{r}{a_0}\right), \tag{189}$$

$$u_{20}(r) = \frac{1}{\sqrt{2}}\left(\frac{1}{a_0}\right)^{1/2} e^{-r/2a_0}\left(\frac{r}{a_0}\right)\left(1-\frac{1}{2}\,\frac{r}{a_0}\right) \tag{190}$$

$$u_{21}(r) = \frac{1}{2\sqrt{6}}\left(\frac{1}{a_0}\right)^{1/2} e^{-r/2a_0}\left(\frac{r}{a_0}\right)^2 \tag{191}$$

$$u_{30}(r) = \frac{2}{3\sqrt{3}}\left(\frac{1}{a_0}\right)^{1/2} e^{-r/3a_0}\left(\frac{r}{a_0}\right)\left(1-\frac{2}{3}\,\frac{r}{a_0}+\frac{2}{27}\left(\frac{r}{a_0}\right)^2\right) \tag{192}$$

$$u_{31}(r) = \frac{8}{27\sqrt{6}}\left(\frac{1}{a_0}\right)^{1/2} e^{-r/3a_0}\left(\frac{r}{a_0}\right)^2\left(1-\frac{1}{6}\,\frac{r}{a_0}\right) \tag{193}$$

$$u_{32}(r) = \frac{4}{81\sqrt{30}}\left(\frac{1}{a_0}\right)^{1/2} e^{-r/3a_0}\left(\frac{r}{a_0}\right)^3 \tag{194}$$

Useful integrals involving the solutions are expectation values like

$$\langle \frac{r^2}{a_0^2} \rangle = \frac{n^2}{2} \left[5n^2 - 3\,\ell(\ell+1) + 1 \right], \tag{195}$$

$$\langle \frac{r}{a_0} \rangle = \frac{1}{2} \left[3\,n^2 - \ell(\ell+1) \right], \tag{196}$$

$$\langle \frac{a_0}{r} \rangle = \frac{1}{n^2}, \tag{197}$$

$$\langle \frac{a_0^2}{r^2} \rangle = \frac{2}{n^3(2\ell+1)}, \tag{198}$$

$$\langle \frac{a_0^3}{r^3} \rangle = \frac{2}{n^3\,\ell(\ell+1)(2\ell+1)}. \tag{199}$$

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.

6 Spin

6.1 Rotational invariance (extended to spinning particles)

As discussed earlier in addition to orbital angular momentum a system, elementary or composite can have a spin, which may include internal orbital angular momentum. Hence spin is a vector operator $\boldsymbol{s}$, which is a part of the rotation operator. These (three) hermitean operators satisfy commutation relations

$$[s_i, s_j] = i\hbar\epsilon_{ijk}\, s_k, \tag{200}$$

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.

For the orbital angular momentum, we have seen the explicit link to spatial rotations, $\ell_z = -i\hbar\,\partial/\partial\varphi$. That means that scalars (e.g. numbers) are not affected. Also operators that do not have azimuthal dependence are not affected, which means for operators that they commute with ℓ_z. The various components of a vector do depend on the azimuthal angle and 'vector operators' such as $\boldsymbol{r}$ or $\boldsymbol{p}$ do not commute with ℓ_z. In fact *scalar* operators S and *vector* operators $\boldsymbol{V}$ satisfy

$$\left.\begin{array}{l}[\ell_i, S] = 0 \\ [\ell_i, V_j] = i\hbar\,\epsilon_{ijk}\, V_k\end{array}\right\} \text{ for a single particle without spin,} \tag{201}$$

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 $\boldsymbol{s}$, this behavior seems to be no longer true, e.g. $[\ell_i, s_j] = 0$ and $[\ell_i, \boldsymbol{\ell}\cdot\boldsymbol{s}] = -i\hbar\,(\boldsymbol{\ell}\times\boldsymbol{s})_i$. But with the 'correct' rotation operator

$$\boldsymbol{j} \equiv \boldsymbol{\ell} + \boldsymbol{s}, \tag{202}$$

we do get

$$\left.\begin{array}{l}[j_i, S] = 0 \\ [j_i, V_j] = i\hbar\,\epsilon_{ijk}\, V_k,\end{array}\right\} \text{ for a single particle} \tag{203}$$

not only for the above examples, but now also for the vectors $\boldsymbol{s}$ and $\boldsymbol{j}$ and 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. Their sums

$$\boldsymbol{L} = \sum_{n=1}^{N} \boldsymbol{\ell}_n, \qquad \boldsymbol{S} = \sum_{n=1}^{N} \boldsymbol{s}_n, \qquad \boldsymbol{J} = \sum_{n=1}^{N} \boldsymbol{j}_n = \boldsymbol{L} + \boldsymbol{S}, \tag{204}$$

also satisfy angular momentum 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

$$\left.\begin{array}{l}[J_i, S] = 0 \\ [J_i, V_j] = i\hbar\,\epsilon_{ijk}\, V_k\end{array}\right\} \text{ for an isolated system} \tag{205}$$

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

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Exercise: Show that from $[J_i, A_j] = i\hbar\,\epsilon_{ijk}\, A_k$ and $[J_i, B_j] = i\hbar\,\epsilon_{ijk}\, B_k$ (satisfying Eq. 205) one finds

$$[J_i, \boldsymbol{A}\cdot\boldsymbol{B}] = 0,$$

i.e. if $\boldsymbol{A}$ and $\boldsymbol{B}$ are vector operators, $\boldsymbol{A}\cdot\boldsymbol{B}$ is a scalar operator. Prove this for J_x without loss of generality.

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An important property is that rotational invariance is one of the basic symmetries of our world, which reflects itself in quantum mechanics as

Rotation invariance of a system of particles requires

$$[\boldsymbol{J}, H] = 0, \tag{206}$$

where $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S} = \sum_i (\boldsymbol{\ell}_i + \boldsymbol{s}_i)$. This is the (generalized, cf. Eq. **??**) fundamental symmetry of nature for particles with spin!

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

6.2 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 $\boldsymbol{s}^2 = s_x^2 + s_y^2 + s_z^2$,

$$[s_i, s_j] = i\hbar\,\epsilon_{ijk}\,s_k, \tag{207}$$

$$[\boldsymbol{s}^2, s_i] = 0. \tag{208}$$

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

$$\boldsymbol{s}^2|s, m\rangle = \hbar^2\,s(s+1)|s, m\rangle, \tag{209}$$

$$\boldsymbol{s}_z|s, m\rangle = m\hbar\,|s, m\rangle. \tag{210}$$

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

$$s_\pm \equiv s_x \pm i\,s_y. \tag{211}$$

The commutation relations for these operators are,

$$[\boldsymbol{s}^2, s_\pm] = 0, \tag{212}$$

$$[s_z, s_\pm] = \pm\hbar\,s_\pm, \tag{213}$$

$$[s_+, s_-] = 2\hbar\,s_z, \tag{214}$$

The first two can be used to show that

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

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

$$\begin{aligned}
s_+|s,m\rangle &= \hbar\sqrt{s(s+1)-m(m+1)}\,|s,m+1\rangle\\
&= = \hbar\sqrt{(s-m)(s+m+1)}\,|s,m+1\rangle \qquad (215)\\
s_-|s,m\rangle &= \hbar\sqrt{s(s+1)-m(m-1)}\,|s,m-1\rangle\\
&= \hbar\sqrt{(s+m)(s-m+1)}\,|s,m-1\rangle. \qquad (216)
\end{aligned}$$

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 215 and 216 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.

6.3 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.

6.4 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

$$|1/2, +1/2\rangle \equiv \chi^{(1/2)}_{+1/2} \equiv \chi_+ \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |1/2, -1/2\rangle \equiv \chi^{(1/2)}_{-1/2} \equiv \chi_- \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Using the definition of the quantum numbers in Eq. 210 one finds that

$$s_z = \hbar \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix}, \quad s_+ = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \quad s_- = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix},$$

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

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

For spin 1 we define the basis states $|1, +1\rangle$, $|1, 0\rangle$ and $|1, -1\rangle$ or

$$\chi^{(1)}_{+1} \equiv \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \qquad \chi^{(1)}_{0} \equiv \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \chi^{(1)}_{-1} \equiv \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

The spin matrices are then easily found,

$$s_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \; s_+ = \hbar \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix}, \; s_- = \hbar \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix},$$

from which also s_x and s_y can be constructed.

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Exercise: Convince yourself that you can do this construction, e.g. by doing it for spin 3/2.

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6.5 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

$$\boldsymbol{s}\cdot\hat{\boldsymbol{n}} = \frac{1}{2}\,\hbar\,\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}} = \frac{\hbar}{2}\begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}. \tag{217}$$

We find the following two eigenstates and eigenvalues

$$\chi_+(\hat{\boldsymbol{n}}) = \begin{pmatrix} \cos(\theta/2) \\ \sin(\theta/2) \end{pmatrix} \qquad \text{with eigenvalue} \quad +\hbar/2,$$
$$\chi_-(\hat{\boldsymbol{n}}) = \begin{pmatrix} -\sin(\theta/2) \\ \cos(\theta/2) \end{pmatrix} \qquad \text{with eigenvalue} \quad -\hbar/2.$$

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

$$\left|\chi_+^\dagger(\hat{\boldsymbol{n}})\chi_\uparrow\right|^2 = \cos^2(\theta/2).$$

Instead of explicitly solving the eigenstates, we of course also can use the rotation operators in quantum mechanics,

$$U(\theta,\hat{\boldsymbol{n}}) = \exp\left(i\,\theta\,\hat{\boldsymbol{n}}\cdot\boldsymbol{J}\right), \tag{218}$$

where $\boldsymbol{J}$ is the total angular momentum operator referred to before in chapter one and in the section on rotation invariance. The total angular momentum operator is the generator of rotations.

A simple example is the rotation of a spin 1/2 spinor. The rotation matrix that brings a spin up state along the z-axis into a spin up state along a rotated direction with polar angle in the $x-z$ plane is[2] is

$$U(\theta) = e^{-i\,\theta\sigma_y/2} = \cos(\theta/2)\,I - i\,\sin(\theta/2)\,\sigma_y.$$

where I is the 2×2 unit matrix.

==========

Exercise: Check that $U(\theta)|1/2,1/2\rangle$ gives the rotated spin state above, while $\boldsymbol{S}\cdot\hat{\boldsymbol{n}} = U(\theta)\,S_z\,U^{-1}(\theta)$.

==========

To find the expansion of any rotated spinor in the original spin states one considers in general the Euler rotations of the form

$$U(\varphi,\theta,-\varphi) = e^{-i\,\varphi\,J_z}\,e^{-i\,\theta\,J_y}\,e^{i\,\varphi\,J_z}$$

Its matrix elements are referred to as the D-functions,

$$\langle j,m'|U(\varphi,\theta,-\varphi)|j,m\rangle = D^{(j)}_{m'm}(\varphi,\theta,-\varphi) = e^{i(m-m')\varphi}\,d^{(j)}_{m'm}(\theta). \tag{219}$$

In general the rotated eigenstates are written as

$$\chi^{(s)}_m(\hat{\boldsymbol{n}}) \;=\; \begin{pmatrix} d^{(s)}_{sm}(\theta) \\ \vdots \\ d^{(s)}_{m'm}(\theta) \\ \vdots \\ d^{(s)}_{-sm}(\theta) \end{pmatrix}. \tag{220}$$

[2]Use the relation $\exp(i\theta\,\hat{\boldsymbol{n}}\cdot\boldsymbol{\sigma}/2) = \cos(\theta/2)\,I + i\,\boldsymbol{\sigma}\cdot n\,\sin(\theta/2)$. Properties of the Pauli matrices can be found in many books.

where $d_{m'm}(\theta)$ are the d-functions. These are in fact just matrix elements of the spin rotation matrix $\exp(-i\,\theta\,J_y)$ between states quantized along the z-direction. Extended to include azimuthal dependence it is necessary to use the rotation matrix $e^{-i\,\varphi\,J_z}\,e^{-i\,\theta\,J_y}\,e^{-i\,\chi\,J_z}$ and the relevant functions are called $D_{m'm}(\varphi,\theta,\chi)$. For integer ℓ one has

$$D^{(\ell)}_{m0}(\varphi,\theta,0) = \sqrt{\frac{4\pi}{2\ell+1}}\,Y^{m*}_{\ell}(\theta,\varphi), \tag{221}$$

$$D^{(\ell)}_{m0}(0,\theta,\varphi) = (-)^m\sqrt{\frac{4\pi}{2\ell+1}}\,Y^{m*}_{\ell}(\theta,\varphi). \tag{222}$$

==========

Exercise: Give the explicit matrix $U(\varphi,\theta,-\varphi)$ for $j = 1/2$.

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7 Combination of angular momenta

7.1 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

$$\boldsymbol{J} = \boldsymbol{j}_1 + \boldsymbol{j}_2. \tag{223}$$

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

$$|j_1, m_1\rangle \otimes |j_2, m_2\rangle, \tag{224}$$

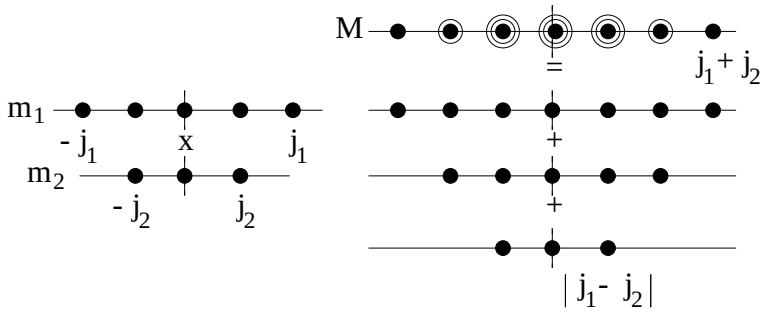
which we can write down since not only $[\boldsymbol{j}_1^2, j_{1z}] = [\boldsymbol{j}_2^2, j_{2z}] = 0$, but also $[j_{1m}, j_{2n}] = 0$. The sum-operator $\boldsymbol{J}$ obviously is not independent, but since the $\boldsymbol{J}$-operators again satisfy the well-known angular momentum commutation 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. 224, $[\boldsymbol{J}^2, j_{1z}] \neq 0$ 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. 224 into states characterized with the quantum numbers

$$|j_1, j_2; J, M\rangle. \tag{225}$$

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

$$J = j_1 + j_2,\ j_1 + j_2 - 1, \ldots, |j_1 - j_2|, \tag{226}$$

going down in steps of one.

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

$$\sum_{J=|j_1-j_2|}^{j_1+j_2} (2J + 1) = (2j_1 + 1)(2j_2 + 1). \tag{227}$$

Furthermore we have in combining angular momenta:

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

7.2 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. 224,

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

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

$$|1/2, 1/2; 1, +1\rangle = |\uparrow\uparrow\rangle. \tag{228}$$

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

$$|1/2,1/2;1,0\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\Big). \tag{229}$$

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

$$|1/2,1/2;1,-1\rangle = |\downarrow\downarrow\rangle. \tag{230}$$

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. 229. 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

$$|1/2,1/2;0,0\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\Big). \tag{231}$$

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.

$j_1 \times j_2$	⋮ J ⋮
	⋮ M ⋮
... ...	
m_1 m_2	
... ...	

For the above case we have

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

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

$$|j_1,j_2;J,M\rangle = \sum_{m_1,m_2} C(j_1,m_1,j_2,m_2;J,M)\,|j_1,m_1\rangle \otimes |j_2,m_2\rangle. \tag{232}$$

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

$$|j_1,m_1\rangle \otimes |j_2,m_2\rangle = \sum_{J,M} C(j_1,m_1,j_2,m_2;J,M)\,|j_1,j_2;J,M\rangle. \tag{233}$$

In some cases (like combining two spin 1/2 states) one can make use of symmetry arguments. If a particular state has a well-defined symmetry under permutation of states 1 and 2, then all M-states belonging to a particular J-value have the same symmetry (because $j_{1\pm} + j_{2\pm}$ does not alter the symmetry. This could have been used for the $1/2 \times 1/2$ case, as the highest total M is symmetric, all $S = 1$ states are symmetric. This is in this case sufficient to get the state in Eq. 229.

We will give two other examples. The first is

$1\times 1/2$		$3/2$ $+3/2$	$3/2$ $+1/2$	$1/2$ $+1/2$	$3/2$ $-1/2$	$1/2$ $-1/2$	$3/2$ $-3/2$
$+1$	$+1/2$	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

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

The second example is

1×1		2 $+2$	2 $+1$	1 $+1$	2 0	1 0	0 0	2 -1	1 -1	2 -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, also illustrates the symmetry of the resulting wave functions.

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Exercise: Repeat the steps outlined for $1/2 \otimes 1/2 = 0 \oplus 1$ for one of the cases above and calculate the CG coefficients.

==========

Exercise: You can find CG coefficients using `ClebschGordan[{j1,m1},{j2,m2},{J,M}]` in Mathematica. Check some examples from previous Tables and construct 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} with $j_1 = 1$ and $j_2 = 3/2$.

==========

Exercise: The table (given below) contains Clebsch-Gordan coefficients for some general cases. Verify at least one of the entries in the first Table. Check the $|l_1, l_2; l, m\rangle = |1, 1; 0, 0\rangle$ state explicitly using our 1×1 calculation above and the Table.

==========

Table 1: Clebsch-Gordan coefficients $\langle j_1, \frac{1}{2}; m_1, m_2 | jm \rangle$

j	$m_2 = \frac{1}{2}$	$m_2 = -\frac{1}{2}$
$j_1 + \frac{1}{2}$	$\left(\frac{j_1+m+\frac{1}{2}}{2j_1+1}\right)^{\frac{1}{2}}$	$\left(\frac{j_1-m+\frac{1}{2}}{2j_1+1}\right)^{\frac{1}{2}}$
$j_1 - \frac{1}{2}$	$-\left(\frac{j_1-m+\frac{1}{2}}{2j_1+1}\right)^{\frac{1}{2}}$	$\left(\frac{j_1+m+\frac{1}{2}}{2j_1+1}\right)^{\frac{1}{2}}$

Table 2: Clebsch-Gordan coefficients $\langle j_1, 1; m_1, m_2 | jm \rangle$

j	$m_2 = 1$	$m_2 = 0$	$m_2 = -1$
$j_1 + 1$	$\left[\frac{(j_1+m)(j_1+m+1)}{(2j_1+1)(2j_1+2)}\right]^{\frac{1}{2}}$	$\left[\frac{(j_1-m+1)(j_1+m+1)}{(2j_1+1)(j_1+1)}\right]^{\frac{1}{2}}$	$\left[\frac{(j_1-m)(j_1-m+1)}{(2j_1+1)(2j_1+2)}\right]^{\frac{1}{2}}$
j_1	$-\left[\frac{(j_1+m)(j_1-m+1)}{2j_1(j_1+1)}\right]^{\frac{1}{2}}$	$\frac{m}{[j_1(j_1+1)]^{\frac{1}{2}}}$	$\left[\frac{(j_1-m)(j_1+m+1)}{2j_1(j_1+1)}\right]^{\frac{1}{2}}$
$j_1 - 1$	$\left[\frac{(j_1-m)(j_1-m+1)}{2j_1(2j_1+1)}\right]^{\frac{1}{2}}$	$-\left[\frac{(j_1-m)(j_1+m)}{j_1(2j_1+1)}\right]^{\frac{1}{2}}$	$\left[\frac{(j_1+m)(j_1+m+1)}{2j_1(2j_1+1)}\right]^{\frac{1}{2}}$

7.3 Recoupling of angular momenta

The possibility of finding in the coupling $j_1 \otimes j_2$ the angular momentum j_3 actually also implies that $j_3 \otimes j_2$ contains j_1, or that $j_1 \otimes j_2 \otimes j_3$ couples to zero. For that purpose one has introduced the 3j-symbol

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix},$$

which is just a notation (no matrix or so!). It has nice symmetry properties and is related to various CG coefficients as $C(j_1, m_1, j_2, m_2; j_3, m_3)$ or $C(j_1, m_1, j_3, m_3; j_2, m_2)$, etc. The proportionality constants turn out to be independent of the magnetic quantum numbers m_i, but do contain typically some factors $\sqrt{2j+1}$ and sign factors $(-)^j$.

Similarly one finds that the recoupling of three momenta to a total momentum J, can be done in different ways with as intermediate steps $j_1 \otimes j_2 \to J_{12}$ or $j_1 \otimes j_3 \to J_{13}$. The recoupling between such different basis states is independent of magnetic quantum numbers with overlap matrix elements being proportional to the Wigner 6j-symbol, denoted

$$\begin{Bmatrix} j_2 & j_1 & J_{12} \\ j_3 & J & J_{13} \end{Bmatrix}.$$

Again the precise form with several factors $\sqrt{2j+1}$ is constructed to exhibit many nice symmetries under the interchange of the angular momenta involved.

The recouplings of four momenta by first recoupling particular pairs are related through 9j-symbols, denoted

$$\begin{Bmatrix} j_1 & j_2 & J_{12} \\ j_3 & j_4 & J_{34} \\ J_{13} & J_{24} & J \end{Bmatrix}.$$

Properties and definitions of these Wigner symbols can be found in e.g. Messiah.

7.4 The Wigner-Eckart theorem

Specific matrix elements of the form $\langle\beta|O|\alpha\rangle$ describe for instance transitions between states α and β. For instance the absorption or emission of a photon in a state α produces the state $O|\alpha\rangle$. The probability that this state is observed as a state $|\beta\rangle$ is

$$\mathrm{Prob}_{\alpha\to\beta} = |\langle\beta|O|\alpha\rangle|^2 .$$

For particular operators O we can make statements on the transition being allowed for specific angular momentum quantum numbers of the states (similar as illustrated for parity).

We first note that for any operator S commuting with the angular momentum operators ($[\boldsymbol{J}, S] = 0$), the quantum numbers are not changed, thus

$$\langle J'M'|S|J,M\rangle \sim \delta_{JJ'}\,\delta_{MM'}. \tag{234}$$

Thus one has $\Delta J = \Delta M = 0$.

A second interesting case are vector operators, for which we also know the commutation relations. It is easy to rewrite these using $J_\pm = J_x \pm i\,J_y$ and $V_\pm = V_x \pm i\,V_y$. One has

$$[J_x, V_\pm] = \mp\hbar V_z, \qquad [J_y, V_\pm] = -i\hbar V_z, \qquad [J_z, V_\pm] = \pm\hbar V_\pm, \tag{235}$$

or using $J_\pm$,

$$[J_+, V_+] = [J_-, V_-] = 0, \qquad [J_\pm, V_\mp] = \pm 2\hbar\, V_z. \tag{236}$$

These can just as in the analysis of angular momentum quantum numbers be used to show that

$$J^2\,\boldsymbol{V}|J,M\rangle = \hbar^2 J(J+1)\,\boldsymbol{V}|J,M\rangle, \tag{237}$$

$$J_z\,V_\pm|J,M\rangle = (M\pm 1)\,\hbar\,V_\pm|J,M\rangle, \tag{238}$$

Thus we have the selection rules stating that one can have nonzero transition probabilities only under specific changes of quantum numbers,

$$\begin{aligned} \text{for } V_z: &\qquad \Delta M = M - M' = 0,\\ \text{for } V_+: &\qquad \Delta M = M - M' = +1,\\ \text{for } V_-: &\qquad \Delta M = M - M' = -1. \end{aligned}$$

Because of the commutation relations with the $\boldsymbol{J}$ operators one refers to this as the 'spherical basis' $V_\ell^m = V_1^m$,

$$V_1^{\pm 1} = \mp\frac{V_x \pm i\,V_y}{\sqrt{2}}, \qquad V_1^0 = V_z. \tag{239}$$

These are chosen such that

$$[J_z, O_\ell^m] = m\,\hbar\,O_\ell^m \quad \text{and} \quad [J_\pm, O_\ell^m] = \hbar\sqrt{\ell(\ell+1) - m(m\pm 1)}\,O_\ell^{m\pm 1}, \tag{240}$$

for which one in general can write

$$\langle J'M'|O_\ell^m|J,M\rangle = C(\ell,m;J,M;J',M')\,\frac{\langle J'||O_\ell||J\rangle}{\sqrt{2J'+1}}. \tag{241}$$

The quantity $\langle J'||O_\ell||J\rangle$ is referred to as reduced matrix element. The most well-known applications of the Wigner-Eckart theorem are its application to the multipole operators describing the interactions of photons with matter, as well as selection rules in interactions between atomic nuclei and elementary particles with different spin states. It reduces $(2J+1)(2\ell+1)(2J'+1)$ matrix elements to *one* reduced matrix element and the use of (tabulated) Clebsch-Gordan coefficients.

Emission and absorption of light

For emission and absorption of light (photons) the relevant operator is the electric dipole operator, which in essence is the position operator, or more precisely the position operator weighted by the charges, $\boldsymbol{D} = \sum_i e_i \boldsymbol{r}_i$. The calculation of transition probabilities are given by the matrix elements between the appropriate states. Since the dipole operator does not involve spin operators, we have $[D_i, S_j] = 0$ and 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.

$$\Delta s = \Delta m_s = 0. \tag{242}$$

In fact the photon polarization determines which of the components of the position operator is the relevant operator. The photon polarizations for linearly polarized light (directed in z-direction) are

$$\text{linear}: \quad \epsilon_x = \hat{x} \quad \text{and} \quad \epsilon_y = \hat{y},$$

or

$$\text{circular}: \ \epsilon_+ = -(\hat{x} + i\,\hat{y})/\sqrt{2} \quad \text{and} \quad \epsilon_- = (\hat{x} - i\,\hat{y})/\sqrt{2}$$

For polarized light we thus precisely get the (spherical) representation of the position vector in terms of the two spherical harmonics with $\ell = 1$,

$$\boldsymbol{r} \cdot \boldsymbol{\epsilon}_{m_\gamma} = \sqrt{\frac{4\pi}{3}}\, r Y_1^{m_\gamma}. \tag{243}$$

We now just can do the explicit calculation

$$\langle 1|\boldsymbol{r} \cdot \boldsymbol{\epsilon}|2\rangle = \sqrt{\frac{4\pi}{3}} \int d^3r\ \psi^*_{n_1\ell_1 m_1}(\boldsymbol{r})\, r\, Y_1^{m_\gamma}(\theta,\varphi)\, \psi_{n_2\ell_2 m_2}(\boldsymbol{r}),$$

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

$$\Delta m_\ell = \pm 1, \tag{244}$$

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 an explicit example of the Wigner-Eckart theorem, and of course precisely follows the general framework pointed out above.

This leads besides the m-selection rule to $|\Delta\ell| \leq 1$ 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

$$\Delta\ell = \pm 1. \tag{245}$$

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

$$\Delta J = 0,\ \pm 1 \tag{246}$$

(with $J = 0 \to J = 0$ 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 $\Delta\ell = 2$.

8 Identical particles

8.1 Permutation symmetry

In many cases, most well-known the case of many electrons in an atom, the Hamiltonian is invariant under *permutations* of the particle labels, $i \leftrightarrow j$, written symbolically as

$$H(1 \dots i \dots j \dots Z) = H(1 \dots j \dots i \dots Z). \tag{247}$$

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

$$\phi^{S/A} = \phi(12) \pm \phi(21), \tag{248}$$

which are also eigenstates with the same energy. These are eigenfunctions of the permutation operator P_{ij}, which interchanges two labels, i.e. $P_{ij}\phi(1 \dots i \dots j \dots) = \phi(1 \dots j \dots i \dots)$ 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,

$$\phi^S = \phi(123) + \phi(213) + \phi(231) + \phi(321) + \phi(312) + \phi(132), \tag{249}$$

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

$$\phi^A = \phi(123) - \phi(213) + \phi(231) - \phi(321) + \phi(312) - \phi(132), \tag{250}$$

(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*. This feature is coupled to the spin of the particles (known as the *spin-statistics connection*): 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

$$\phi^A(123) \propto \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_a(1) & \phi_a(2) & \phi_a(3) \\ \phi_b(1) & \phi_b(2) & \phi_b(3) \\ \phi_c(1) & \phi_c(2) & \phi_c(3) \end{vmatrix}.$$

Note that only when the states a, b and c are orthonormal, the normalization is $1/\sqrt{3!}$.

==========

Exercise: Two (one-dimensional) particles can be in orthonormal states a or b.

(a) If the two particles are distinguishable and particle 1 is in state a, while particle 2 is in state b, the wave function can be denoted

$$\phi(x_1, x_2) = \phi_a(x_1)\phi_b(x_2) \quad \text{or} \quad |\phi\rangle = |ab\rangle = |a\rangle \otimes |b\rangle.$$

Determine the (normalized) two-body wave function $\phi(x_1, x_2)$ if (i) the particles are indistinguishable bosons; (ii) the particles are indistinguishable fermions.

(b) Show that for distinguishable particles the expectation value of the distance squared is given by

$$\langle\phi|x_1^2 + x_2^2 - 2x_1x_2|\phi\rangle = \left(\langle x\rangle_a - \langle x\rangle_b\right)^2 + (\Delta x)_a^2 + (\Delta x)_b^2$$

Express in the same way this expectation value in terms of matrix elements for the states ϕ_a and ϕ_b for cases (i) and (ii) under (a)

(c) Explain from the answer in (b) that identical bosons tend to attract each other, while identical fermions tend to repel each other.

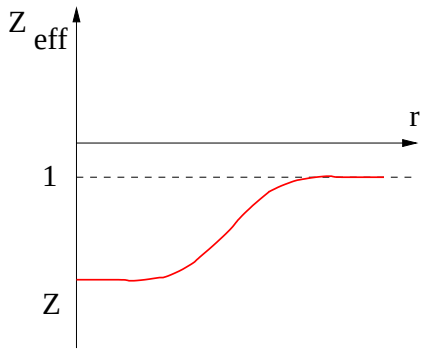
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8.2 Atomic structure

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 the many-electron Hamiltonian

$$H(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_Z; \boldsymbol{p}_1, \ldots, \boldsymbol{p}_Z) = \sum_{i=1}^{Z} \left(-\frac{\hbar^2}{2m}\,\boldsymbol{\nabla}_i^2 - \frac{Ze^2}{4\pi\epsilon_0\, r_i} \right) + \sum_{i>j}^{Z} \frac{e^2}{4\pi\epsilon_0\, |\boldsymbol{r}_i - \boldsymbol{r}_j|} \tag{251}$$

by an effective central potential. The effective charge felt by an electron is expected to behave like

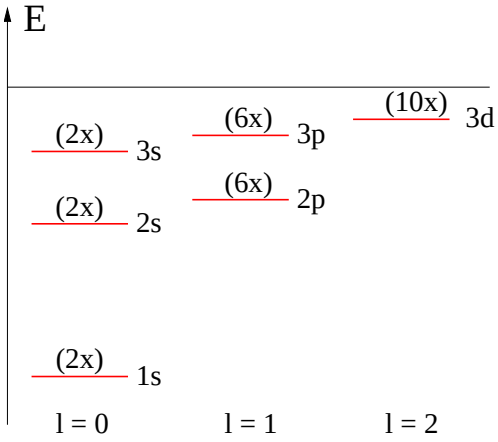


$$Z_{\rm eff} \begin{cases} \stackrel{r\to\infty}{\longrightarrow} 1 \\ \stackrel{r\to 0}{\longrightarrow} Z \end{cases}$$

The behavior of $Z_{\rm eff}(r)$ can e.g. be obtained from the electron densities in a self-consistent matter. Thus, one can approximate the many-electron hamiltonian by

$$H(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_Z;\boldsymbol{p}_1,\ldots,\boldsymbol{p}_Z) \approx \sum_{i=1}^{Z}\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}_i^2 - \frac{Z_{\rm eff}(r)\,e^2}{4\pi\epsilon_0\,r_i}\right) + \ldots \tag{252}$$

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, 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 $Z_{\rm eff}(r)$. The only effect of the latter is the splitting of different ℓ-values corresponding to the same principal quantum number n.

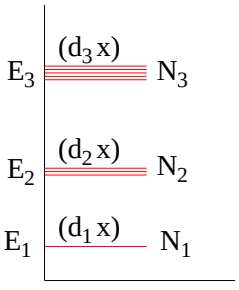
The structure of the periodic table is summarized in the table given below with the levels given in order of increasing energy. In this table the noble gases correspond to situations in which there are large

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 #	
1	2	3	4	5	6	7	of levels	remarks
$(1s)^2$							2 (He)	
	$(2s)^2$ $(2p)^6$						4 10 (Ne)	
		$(3s)^2$ $(3p)^6$					12 18 (Ar)	
		$(3d)^{10}$	$(4s)^2$ $(4p)^2$				20 30 36 (Kr)	Fe-group
			$(4d)^{10}$	$(5s)^2$ $(5p)^6$			38 48 54 (Xe)	Pd-group
			$(4f)^{14}$	$(5d)^{10}$	$(6s)^2$ $(6p)^6$		56 70 80 86 (Rn)	Lanthanides Pt-group
				$(5f)^{14}$	$(6d)^{10}$	$(7s)^2$ $(7p)^6$	88 102 112 118 (?)	Actinides Pt-group

8.3 Quantum statistics

When we have a large number of particles (gases, liquids) they in principle occupy available levels. The guiding principle is the equipartition theorem, which is the assumption that all states with the same total energy have equal probability. Extreme states, e.g. all particles in the ground state and a single one occupying a very high level to achieve a particular configuration with high energy is then one out of an almost infinite set, while the groundstate with all particles in the lowest state is one out of one possibility. To deal with this one introduces *temperature*, which is nothing else than the average energy per degree of freedom (modulo a constant, the Boltzmann constant, which is just defining the temperature scale).



Consider a situation in which a particular level with energy E_n, which has a degeneracy d_n, is occupied by N_n particles. The total number of particles is $N = \sum_n N_n$, the total energy is $E = \sum_n N_n E_n$. The challenge of quantum statistics is to do the proper counting for distinguishable particles (a) or for identical particles in the case of fermions (b) or bosons (c). In all of these cases one needs the number $Q(N_1, N_2, \ldots)$, which is the number of different ways to obtain *one* particular configuration such as shown in the figure left.

This is worked out for example in Griffith's and we have

$$Q(N_1, N_2, \ldots) = N! \prod_n \frac{d_n^{N_n}}{N_n!} \qquad \text{(distinguishable particles)}, \tag{253}$$

$$Q(N_1, N_2, \ldots) = \prod_n \left(\begin{array}{c} d_n \\ N_n \end{array} \right) = \prod_n \frac{d_n!}{N_n!(d_n - N_n)!} \qquad \text{(indistinguishable fermions)}, \tag{254}$$

$$Q(N_1, N_2, \ldots) = \prod_n \left(\begin{array}{c} N_n + d_n - 1 \\ N_n \end{array} \right) = \prod_n \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!} \qquad \text{(indistinguishable bosons)} \tag{255}$$

To put in constraints of a given total energy and/or a given total number of particles, one adds *Lagrange multipliers* and minimizes with respect to the parameters, which are identified with temperature and chemical potential, respectively. That is, one looks for the stationary point by varying

$$G \equiv \ln Q(N_1, N_2, \ldots) + \alpha \left[N - \sum_n N_n \right] + \beta \left[E - \sum_n N_n \, E_n \right], \tag{256}$$

with respect to the N_n's and

$$\beta \equiv \frac{1}{k_B \, T} \quad \text{and} \quad \alpha \equiv -\frac{\mu(T)}{k_B \, T}. \tag{257}$$

The result, assuming that $d_n \gg N_n$ and using Stirling's formula $\ln z! \approx z \, \ln z - z$, gives the most probable configuration for the three cases,

$$N_n = \frac{d_n}{e^{(\alpha + \beta \, E_n)}} \qquad \text{(distinguishable particles)}, \tag{258}$$

$$N_n = \frac{d_n}{e^{(\alpha + \beta \, E_n)} + 1} \qquad \text{(indistinguishable fermions)}, \tag{259}$$

$$N_n = \frac{d_n - 1}{e^{(\alpha + \beta \, E_n)} - 1} \qquad \text{(indistinguishable bosons)}. \tag{260}$$

The introduction of temperature (parameter β) is the most important one. The Boltzmann constant $k_B = 1.38 \times 10^{-23}$ J/K $= 8.6 \times 10^{-5}$ eV/K, just sets the temperature scale. In cases in which the number of particles is not conserved (e.g. photons), one omits the introduction of α, and the result is the same with $\alpha = 0$.

Quantum gases

The most well-known application are the levels in a volume V for free particles. The quantum states are plane waves of which the density of states in momentum space is given by

$$d_k = d(\boldsymbol{k}) \, d^3k = \frac{1}{\rho} \, \frac{d^3k}{(2\pi)^3}. \tag{261}$$

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,

$$\mathbf{1} = \int d^3r \; |\boldsymbol{r}\rangle \, \langle \boldsymbol{r}| = \frac{1}{\rho} \int \frac{d^3k}{(2\pi)^3} \; |\boldsymbol{k}\rangle \, \langle \boldsymbol{k}|.$$

Another way is to use box normalization, in which case one finds that for one particle in a box with sides L, i.e. $0 \leq x \leq L$, $0 \leq y \leq L$ and $0 \leq z \leq L$ (i.e. density $\rho = 1/L^3$), the wave function is found after imposing periodic boundary conditions,

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

with $\boldsymbol{k} = (2\pi/L)\,(n_x, n_y, n_z)$, showing a density of states in k-space given by $(L/2\pi)^3$. Rewriting the density of states $d(\boldsymbol{k})$ in terms of k and Ω_k or E and Ω_k we find for the degeneracy

$$d_k = d(\boldsymbol{k}) d^3k = \frac{1}{\rho}\,\frac{k^2}{(2\pi)^3}\,dk\,d\Omega. \tag{262}$$

Integrating over the spherically symmetric $\boldsymbol{k}$-space and putting in the volume, $\rho = 1/V$, one gets,

$$d_k = \frac{V}{2\pi^2}\,k^2\,dk = d(k)\,dk \quad \text{or} \quad d_E = \frac{V}{4\pi^2}\,\left(\frac{2m}{\hbar^2}\right)^{3/2}\,\sqrt{E}\,dE \tag{263}$$

Thus for a gas one gets (take $\alpha = 0$) the energy

$$E = \frac{V}{4\pi^2}\,\left(\frac{2m}{\hbar^2}\right)^{3/2} \int dE\; E^{3/2}\,\exp(-\beta\,E) = V\,\frac{3}{2}\left(\frac{m}{2\pi\,\beta\,\hbar^2}\right)^{3/2} \tag{264}$$

(using $\int dx\; x^{n-1}\,e^{-x} = \Gamma(n)$ satisfying $\Gamma(n+1) = n\,\Gamma(n) = n!$ and $\Gamma(1/2) = \sqrt{\pi}$, thus $\Gamma(3/2) = \sqrt{\pi}/2$ and $\Gamma(5/2) = 3\sqrt{\pi}/4$). Including the constraint for N one gets

$$N = V\,e^{-\alpha}\left(\frac{2m}{2\pi\,\beta\,\hbar^2}\right)^{3/2}, \tag{265}$$

$$E = V\,\frac{3}{2}\,e^{-\alpha}\left(\frac{m}{2\pi\,\beta\,\hbar^2}\right)^{3/2}, \tag{266}$$

satisfying (with $\beta = 1/k_BT$) the well-known relation

$$E = \frac{3}{2}\,N\,k_BT, \tag{267}$$

and for which we have for the chemical potential

$$e^{-\alpha} = \exp(\mu(T)/k_BT) = \frac{N}{V}\left(\frac{2\pi\,\beta\,\hbar^2}{m}\right)^{3/2}. \tag{268}$$

The occupancies thus are

$$n(E) = \frac{N_E}{d_E} = \frac{1}{e^{(E-\mu)/k_BT} + c}. \tag{269}$$

with $c = 0$ for a gas of distinguishable particles (Maxwell-Boltzmann distribution), $c = +1$ for a gas of indistinguishable fermions (Fermi-Dirac distribution) and $c = -1$ for a gas of indistinguishable bosons (Bose-Einstein distribution).

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Exercise: Show that for a Fermi-Dirac distribution one has at $T = 0$ that $n(E < E_F) = 1$ and $n(E > E_F) = 0$, where $E_F = \mu(0)$.

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Exercise: Derive the Planck distribution of photons at a given temperature, using the energy and momentum relation for photons, $E = \hbar\,\omega$ and $k = \omega/c$ and show that the energy density is

$$\mathcal{E}(\omega, T) = \frac{\hbar\,\omega^3}{\pi^2\,c^3}\,\frac{1}{e^{\hbar\omega/k_BT} - 1}.$$

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Exercise: Calculate the density of photons in the universe from the temperature of the cosmic microwave background, $T = 2.725$ K.

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Exercise: Study the relativistic version of Eq. 262 - 268.

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9 Spin and permutation symmetry in Atomic Physics

9.1 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,

$$\phi^{s/a}_{LM_L} = \frac{1}{\sqrt{2}}\left[\frac{u_{1s}(r_1)}{r_1}\,Y^0_0(\Omega_1)\,\frac{u_{2p}(r_2)}{r_2}\,Y^{M_L}_1(\Omega_2) \pm \frac{u_{2p}(r_1)}{r_1}\,Y^{M_L}_1(\Omega_1)\frac{u_{1s}(r_2)}{r_2}\,Y^0_0(\Omega_2)\right]$$

    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,

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

- 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

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

We summarize the result in tabular form including the $(2p)^2$ configuration and indicating which states are not allowed because of the Pauli principle. To find out which states are forbidden, we indicated the symmetry of the orbital part of the wave function (L) as well as the symmetry of the spin part $((S)$ for symmetric, (A) for anti-symmetric).

Configurations in Helium							
configuration	$E^{(0)}/R_\infty$	Parity	L	S	^{2S+1}L terms	J-values	# states
$(1s)^2$	-8	+	0 (S)	0 (A)	$(1s)^2\ ^1S$	$^1S_0$	1
				1 (S)	$(1s)^2\ ^3S$	not allowed	3
$(1s)(2p)$ & $(2p)(1s)$	-5	−	1(A)	0 (A)	$(1s)(2p)\,^1P$	not allowed	3
				1 (S)	$(1s)(2p)^3P$	$^3P_0$, $^3P_1$, $^3P_2$	9
			1(S)	0 (A)	$(1s)(2p)\,^1P$	$^1P_1$	3
				1 (S)	$(1s)(2p)\,^3P$	not allowed	9
$(1s)(2s)$ & $(2s)(1s)$	-5	+	0 (A)	0(A)	$(1s)(2s)\,^1S$	not allowed	1
				1(S)	$(1s)(2s)\,^3S$	$^3S_1$	3
	-5	+	0 (S)	0(A)	$(1s)(2s)\,^1S$	$^1S_0$	1
				1(S)	$(1s)(2s)\,^3S$	not allowed	3
$(2p)^2$	-2	+	0 (S)	0 (A)	$(2p)^2\ ^1S$	$^1S_0$	1
				1 (S)	$(2p)^2\ ^3S$	not allowed	3
			1 (A)	0 (A)	$(2p)^2\ ^1P$	not allowed	3
				1 (S)	$(2p)^2\ ^3P$	$^3P_0$, $^3P_1$, $^3P_2$	9
			2 (S)	0 (A)	$(2p)^2\ ^1D$	$^1D_2$	5
				1 (S)	$(2p)^2\ ^3D$	not allowed	15

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.

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Exercise: Including the ee-interaction the Hamiltonian for 2 electrons in an atom (see Eq. 251) is no longer the sum of two Hydrogenlike Hamiltonians. The electron-electron interaction term breaks the factorization. Omitting the term H_{12} one can write down the wave function as a product of $(1s)$ wave functions. For this product wave function, the expectation value is

$$E^{(0)} = \langle (1s)^2 | H_1 + H_2 | (1s)^2 \rangle = -2\, Z^2\, R_\infty,$$

which is for Helium $E^{(0)} = -8\, R_\infty$, the zeroth order approximation of the $(1s)^2\ ^1S_0$ groundstate. A way to account for the ee-interaction is by just adding the H_{12} term to the Hamiltonian, but stick to the approximate wave function.

(a) Calculate for the product of two $(1s)$ waves the expectation value $\Delta E_{\rm gs} = \langle (1s)^2 | H_{12} | (1s)^2 \rangle$ and show that the result is

$$\Delta E_{\rm gs} = \frac{5}{4}\, Z\, R_\infty.$$

(we will encounter this procedure as the first order in perturbation theory). Compare the resulting energy with the experimental value $E_{\rm gs} = -5.81\, R_\infty$.
A useful integral is $\int_0^\infty dx\ x^n\, e^{-\alpha x} = n!/\alpha^{n+1}$ for n integer.

For the next multiplets one has a spatially symmetric or antisymmetric wave function of the form $\psi = \psi_1 \pm \psi_2$, the sign determining the spatial symmetry and the particular spin wave function with which to combine the spatial part.

(b) Express the expectation energy of the Hamiltonian for the (normalized) symmetric and antisymmetric wave functions in terms of the following integrals

$$\begin{aligned}
&\langle\psi_1|\psi_1\rangle = \langle\psi_2|\psi_2\rangle = 1 \quad \psi_1 \text{and } \psi_2 \text{ (assumed normalized)},\\
&\langle\psi_1|H_i|\psi_1\rangle = E_i^{(0)} \qquad (\text{i} = 1,2),\\
&\langle\psi_1|\psi_2\rangle = \langle\psi_2|\psi_1\rangle = S \qquad (\text{overlap integral}),\\
&\\
&\langle\psi_1|H_{12}|\psi_1\rangle = \langle\psi_2|H_{12}|\psi_2\rangle = C \qquad (\text{Coulomb integral}),\\
&\langle\psi_1|H_{12}|\psi_2\rangle = \langle\psi_2|H_{12}|\psi_1\rangle = K \qquad (\text{exchange integral}).
\end{aligned}$$

(c) Looking at the $(1s)(2p)$ and $(1s)(2s)$ configurations the Coulomb integral is smallest for $(1s)(2s)$ (could you think of a reason), while the exchange integral is positive. Sketch the spectrum of Helium including the lowest para-Helium and ortho-Helium states and indicate some of the allowed radiative dipole transitions.

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9.2 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 $^2P \rightarrow^2 S$ 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 $^2P_{3/2} \rightarrow^2 S_{1/2}$ and $^2P_{1/2} \rightarrow^2 S_{1/2}$. 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

0	0	0	0	0
1	1	1	1	1
0	0	0	0	0

$(L,S)=(2,0)$ +

0	1	1	1	0
0	1	1	1	0
0	1	1	1	0

$(L,S)=(1,1)$ +

0	0	0	0	0
0	0	1	0	0
0	0	0	0	0

$(L,S)=(0,0)$

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

$$E(^3P) < E(^1D) < E(^1S).$$

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Exercise:

(a) Construct the possible multiplets (spectroscopic terms) of a Barium atom in a (6p)(5d) state. Give the degeneracy of each of the terms and check that there are (as expected) 60 states. Use the Hund rules to order the states.

(b) Construct the multiplets for all possible $(np)^N$ configurations of electrons in an atom and give their ordering in energy.

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Exercise: Another system is that consisting of two nucleons, proton-proton, proton-neutron or neutron-neutron. Nucleons have spin 1/2, hence are fermions. They interact with each other through a potential of the form

$$V = V_1(r) + V_2(r)\, \boldsymbol{s}_1 \cdot \boldsymbol{s}_2 + V_3(r) \left[\frac{3(\boldsymbol{s}_1 \cdot \boldsymbol{r})(\boldsymbol{s}_2 \cdot \boldsymbol{r})}{r^2} - \boldsymbol{s}_1 \cdot \boldsymbol{s}_2 \right],$$

where $\boldsymbol{r}$ is the relative coordinate.

- Omitting V_3, what are the good quantum numbers? Give the various $^{(2S+1)}\ell_J$ quantum numbers for pp, pn and nn. Include parity.
- Which of these quantum numbers remain good quantum numbers including the V_3 term?

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Exercise: Because of the similarity of the interaction for protons and neutrons, they are often considered as a nucleon with two possible isospin states $|p\rangle$ and $|n\rangle$ in analogy to spin states (thus isospin 1/2). Construct the isospin 0 and isospin 1 states. What is their symmetry. Show that one can use permutation symmetry including isospin as a degree of freedom and get the same allowed quantum numbers for the two-nucleon system.

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10 Bound state perturbation theory

10.1 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

$$E_n = E_n^{(0)} + \lambda\, E_n^{(1)} + \lambda^2\, E_n^{(2)} + \ldots, \tag{270}$$

$$|\psi_n\rangle = |\phi_n\rangle + \lambda\,|\psi_n^{(1)}\rangle, \tag{271}$$

into the Schrödinger equation $(H - E_n)|\psi_n\rangle = 0$,

$$\big(H_0 + \lambda\, V\big)\big(|\phi_n\rangle + \lambda\,|\psi_n^{(1)}\rangle + \ldots\big) = \big(E_n^{(0)} + \lambda\, E_n^{(1)} + \ldots\big)\big(|\phi_n\rangle + \lambda\,|\psi_n^{(1)}\rangle + \ldots\big). \tag{272}$$

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

$$\lambda\, V|\phi_n\rangle + \lambda\, H_0|\psi_n^{(1)}\rangle = \lambda\, E_n^{(1)}|\phi_n\rangle + \lambda\, E_n^{(0)}|\psi_n^{(1)}\rangle. \tag{273}$$

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

$$\lambda\, E_n^{(1)} = \langle\phi_n|\lambda\, V|\phi_n\rangle, \tag{274}$$

$$\lambda\big(E_n^{(0)} - E_m^{(0)}\big)\langle\phi_m|\psi_n^{(1)}\rangle = \langle\phi_m|\lambda\, V|\phi_n\rangle \quad (\text{for } m \neq n). \tag{275}$$

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,

$$E_n^{(1)} = \langle\phi_n|V|\phi_n = V_{nn}, \tag{276}$$

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n} |\phi_m\rangle\, \frac{\langle\phi_m|V|\phi_n\rangle}{E_n^{(0)} - E_m^{(0)}} = \sum_{m\neq n} |\phi_m\rangle\, \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}}. \tag{277}$$

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. 272, giving

$$H_0|\psi_n^{(2)}\rangle + V|\psi_n^{(1)}\rangle = E_n^{(0)}|\psi_n^{(2)}\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle + E_n^{(2)}|\phi_n\rangle. \tag{278}$$

Taking the scalar product with $\langle\phi_n|$ gives the result

$$E_n^{(2)} = \langle\phi_n|V|\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{V_{nm}\, V_{mn}}{E_n^{(0)} - E_m^{(0)}}. \tag{279}$$

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

$$\sum_{m\neq n} \Rightarrow \sum_{m\neq n} + \int_0^\infty dE\, \rho(E), \tag{280}$$

where the integral covers the continuum spectrum in which $\rho(E)\, dE$ is the number of states in an energy interval dE around E.

10.2 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. 275 to 277 cannot be made. Eq. 275, however, also tells us how to proceed. Make sure that each subset of states $|\phi_{n1}\rangle, \ldots, |\phi_{ns}\rangle$ 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. 277 the result

$$|\psi_n^{(1)}\rangle = \sum_{E_m^{(0)} \neq E_n^{(0)}} |\phi_m\rangle \frac{\langle\phi_m|V|\phi_n\rangle}{E_n^{(0)} - E_m^{(0)}}. \tag{281}$$

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. One needs to diagonalize the degenerate subspace. This assures that within that subspace the off-diagonal matrix elements are zero and the steps towards obtaining $|\psi_n^{(1)}\rangle$ can be made.

10.3 Applications in Hydrogen

In the hydrogen atom there are a number of additional terms in the hamiltonian that can be attributed to relativistic corrections,

$$H = H_0 + H_{\text{mass}} + H_{\text{Foldy}} + H_{\text{so}} \tag{282}$$

The first term is a correction coming from the difference of the relativistic and nonrelativistic kinetic energies, the *mass term*,

$$H_{\text{mass}} = \sqrt{\boldsymbol{p}^2c^2 + m^2c^4} - mc^2 - \frac{\boldsymbol{p}^2}{2m} \approx -\frac{\boldsymbol{p}^4}{8m^3c^2}. \tag{283}$$

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[3],

$$\Delta E_{\text{mass}}(n\ell) = \langle n\ell m \ldots| - \frac{\boldsymbol{p}^4}{8m^3c^2}|n\ell m \ldots\rangle = -\alpha^2 \frac{R_\infty}{n^3}\left(\frac{1}{\ell + \frac{1}{2}} - \frac{3}{4n}\right). \tag{284}$$

Another interaction term arises because of the interaction of the spin with the induced magnetic field by the orbital motion, the *spin-orbit interaction*. It can be up to a factor 2 be derived with classical arguments, but a proper derivation requires the use of the relativistic Dy spectrumirac equation for the electron. The result for a particle in a central potential is

$$H_{\text{so}} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV_c}{dr}\boldsymbol{\ell}\cdot\boldsymbol{s}. \tag{285}$$

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

$$\boldsymbol{\ell}\cdot\boldsymbol{s} = \frac{1}{2}\left[\boldsymbol{j}^2 - \boldsymbol{\ell}^2 - \boldsymbol{s}^2\right],$$

[3]The calculation is treated in many quantum mechanics books, usually done by rewriting $(\boldsymbol{p}^2)^2 = 4m^2(H - V(r))^2$. This symmetric treatment avoids problems with non-hermiticity of $\boldsymbol{p}^4$ because of boundary terms at $r = 0$

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 $|n\ell sjm\rangle$, 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

$$\begin{aligned}\Delta E_{\rm so}(n\ell sjm) &= \frac{1}{2m^2c^2}\langle n\ell sjm|\frac{1}{r}\frac{dV_c}{dr}\,\boldsymbol{\ell}\cdot\boldsymbol{s}|n\ell sjm\rangle \\ &= \frac{e^2\,\hbar^2}{32\pi\epsilon_0\,m^2c^2}\,\langle n\ell|\frac{1}{r^3}|n\ell\rangle\;[j(j+1)-\ell(\ell+1)-s(s+1)] \\ &= \frac{e^2\,\hbar^2}{32\pi\epsilon_0\,m^2c^2}\,\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{a_0^3\,n^3\,\ell(\ell+1)(\ell+\frac{1}{2})} \end{aligned} \tag{286}$$

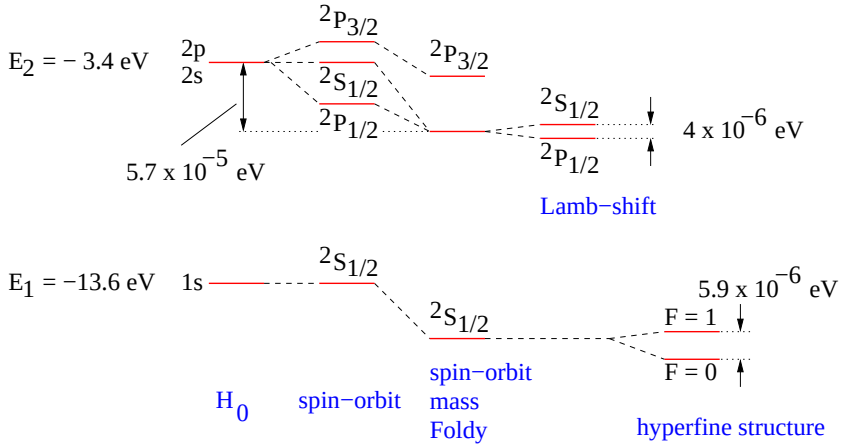
We thus must couple ℓ and s to j-eigenstates. For one electron with a given $\ell \neq 0$ there are two possibilities for j, namely $j = \ell \pm \frac{1}{2}$ giving for $\ell \neq 0$

$$\Delta E_{\rm so}(n\ell j) = \alpha^2\,\frac{R_\infty}{n^3}\left(\frac{1}{\ell+\frac{1}{2}} - \frac{1}{j+\frac{1}{2}}\right) \tag{287}$$

and for the combined result

$$\Delta E_{\rm mass\,+\,so} = -\alpha^2\,\frac{R_\infty}{n^3}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right) \tag{288}$$

In the Hydrogen atom one also has the *Foldy term*, which also is a relativistic correction. It is proportional to $\delta^3(\boldsymbol{r})$ and thus only affects s-waves. It makes the above equation valid also for s-waves. We return to this later. 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

$$V_{ss} = \frac{1}{6\pi\epsilon_0\, c^2}\, \boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_p\, \boldsymbol{\nabla}^2\, \frac{1}{r}. \tag{289}$$

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

$$\Delta E_{ss} \propto g_e\, g_p\, \langle|\boldsymbol{S}\cdot\boldsymbol{I}|\rangle = \frac{1}{2}\, g_e\, g_p\, \hbar^2\, \left[F(+F1) - S(S+1) - I(I+1)\right]. \tag{290}$$

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.

10.4 The fine structure of atoms

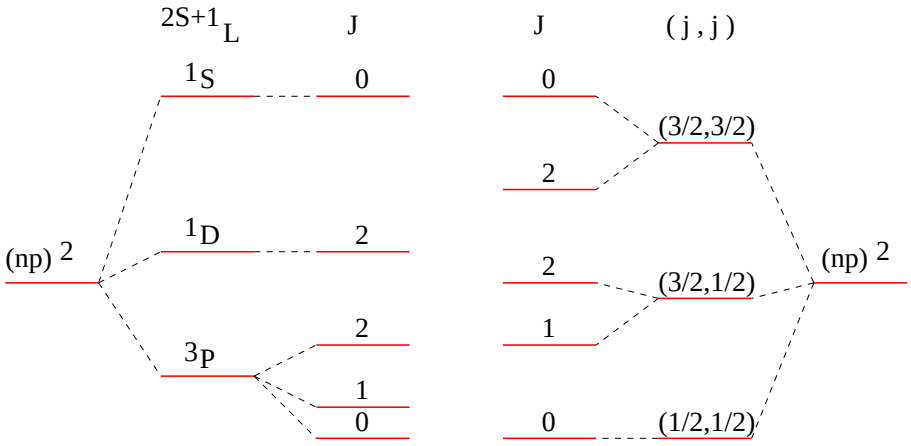
When combining angular momenta, we discussed the multiplets forming the fine structure in atoms. For not too heavy atoms, the splitting of energies within the multiplets turn out to be described well by a spin-orbit interaction of the form

$$H_{\rm so} = A(L,S)\, \boldsymbol{L}\cdot\boldsymbol{S}, \tag{291}$$

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

$$\Delta E(LSJM) = \frac{1}{2}\, A\hbar^2\, \left[J(J+1) - L(L+1) - S(S+1)\right]. \tag{292}$$

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

$$r = \frac{E(^{2S+1}L_J) - E(^{2S+1}L_{J-1})}{E(^{2S+1}L_{J-1}) - E(^{2S+1}L_{J-2})} = \frac{J}{J-1}, \tag{293}$$

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, that works in some cases better for heavy atoms, 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, in which case the interaction is

$$H_{\rm jj} = A(j_1, j_2)\, \boldsymbol{j}_1 \cdot \boldsymbol{j}_2, \tag{294}$$

and the splitting is given by

$$\Delta E(j_1 j_2 J M) = \frac{1}{2}\, A\hbar^2 \left[J(J+1) - j_1(j_1+1) - j_2(j_2+1)\right]. \tag{295}$$

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 $J = 2\,j$ is symmetric, for the next lower J it is antisymmetric, then again symmetric, etc. This explains the J-values in the jj-coupling scheme. After having done all recouplings and accounting for permutation symmetry, the same J-values must appear in both schemes.

11 Magnetic effects in atoms and the electron spin

11.1 The Zeeman effect

Interaction of orbital angular momentum with magnetic field

In a magnetic field an additional interaction is added to the hamiltonian,

$$H = \underbrace{-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \frac{Ze^2}{4\pi\epsilon_0\, r}}_{H_0} + V_{\rm mag}, \tag{296}$$

where $V_{\rm mag} = -\boldsymbol{\mu}\cdot B$. Neglecting spin, the magnetic moment of a particle in orbit is given by

$$\boldsymbol{\mu}_\ell = -g_\ell\,\frac{e}{2m}\,\boldsymbol{\ell} \tag{297}$$

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

$$\Delta E_{n\ell m_\ell} = \langle n\ell m_\ell|\frac{eB}{2m}\,\ell_z|n\ell m_\ell\rangle = m_\ell\,\mu_B B, \tag{298}$$

where

$$\mu_B = \frac{e\hbar}{2m} = \frac{1}{2}\,e\,c\,\frac{\hbar}{mc} \approx 5.8\times10^{-5}\ \text{eV/T} \tag{299}$$

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.

$$V_{\rm mag} = -\boldsymbol{\mu}_s\cdot\boldsymbol{B}, \tag{300}$$

with

$$\boldsymbol{\mu}_s = -g_s\,\frac{e}{2m}\,\boldsymbol{s} = -g_s\,\frac{e\hbar}{m}\,\boldsymbol{\sigma}. \tag{301}$$

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

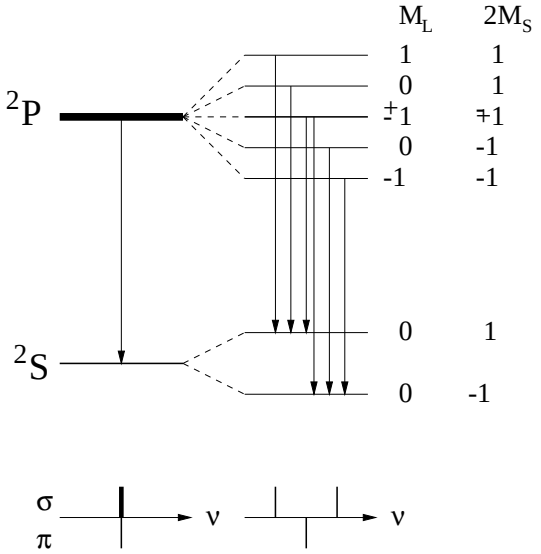
In general a ^{2S+1}L level in a magnetic field is split by an interaction term

$$V_{\rm mag} = -\boldsymbol{\mu} \cdot \boldsymbol{B}, \tag{302}$$

where $\boldsymbol{\mu} = -\mu_B(g_L\,\boldsymbol{L} + g_S\,\boldsymbol{S})$, resulting in a number of levels with the splitting given by

$$\Delta E(LSM_LM_S) = -\mu_B B(M_L + 2\,M_S). \tag{303}$$

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.

11.2 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

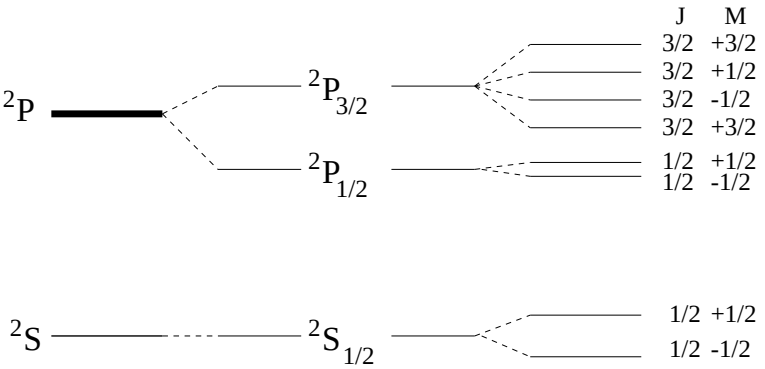
$$H_{\rm int} = A\,\boldsymbol{L} \cdot \boldsymbol{S} - \boldsymbol{\mu} \cdot \boldsymbol{B}, \tag{304}$$

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 $^2P \to ^2S$ 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

$$\Delta E_{\rm mag} = \mu_B B \,\langle(\ldots)LSJM|L_z + 2S_z|(\ldots)LSJM\rangle = \mu_B B \,\langle(\ldots)LSJM|J_z + S_z|(\ldots)LSJM\rangle. \quad (305)$$

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

$$\langle LSJM|S_z|LSJM\rangle = M\,\frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (306)$$

which follows from a subtle relation involving $\boldsymbol{S}$ and $\boldsymbol{J}$ operators[4], $\boldsymbol{J}^2 S_z + S_z \boldsymbol{J}^2 = 2\,J_z\,(\boldsymbol{J}\cdot\boldsymbol{S})$ leading to

$$\Delta E_{\rm mag} = \underbrace{\left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}\right]}_{g_J} M\,\mu_B B, \quad (307)$$

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.

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Exercise:

(a) Use for the ^2P states the basis states $|L, S; M_L, M_S\rangle$ and write down the spin-orbit hamiltonian $H_{\rm so} = A\,\boldsymbol{L}\cdot\boldsymbol{S}$ as a matrix. Use for this the explicit expression

$$H_{\rm so} = \frac{A}{2}\,(2\,L_zS_z + L_+S_- + L_-S_+)\,.$$

Determine the eigenvalues and eigenstates. The latter are of course precisely the $|L, S; J, M\rangle$ states.

[4]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 $[\boldsymbol{J}^2, [\boldsymbol{J}^2, A_i]] = 2\hbar^2(\boldsymbol{J}^2A_i + A_i\boldsymbol{J}^2) - 4\hbar^2(\boldsymbol{A}\cdot\boldsymbol{J})J_i$. For the proof one also needs to realize that between $\boldsymbol{J}^2$ eigenstates the expectation value $\langle JM|[\boldsymbol{J}^2, O]|JM\rangle = 0$ for any operator.

(b) On the same basis, write down the hamiltonian in an external magnetic field, $H_{\rm int} = A\,\boldsymbol{L}\cdot\boldsymbol{S} - \boldsymbol{\mu}\cdot\boldsymbol{B}$, using the explicit form

$$H_{\rm int} = \frac{A}{2}\left(2\,L_z S_z + L_+ S_- + L_- S_+\right) - \mu_B\,B_0\left(L_z + 2\,S_z\right).$$

Find all eigenvalues and check that they coincide with the approximations made for small and large B-fields.

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12 Variational approach

12.1 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,

$$E_{[\alpha_1,\alpha_2,\ldots]} = \frac{\langle\psi_{[\alpha_1,\alpha_2,\ldots]}|H|\psi_{[\alpha_1,\alpha_2,\ldots]}\rangle}{\langle\psi_{[\alpha_1,\alpha_2,\ldots]}|\psi_{[\alpha_1,\alpha_2,\ldots]}\rangle}. \tag{308}$$

If the true solutions and energies of H are given by $(H - E_n)\,|\phi_n\rangle = 0$, it is simple to show that

$$E_{[\alpha_1,\alpha_2,\ldots]} \geq E_0, \tag{309}$$

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,

$$\frac{\partial E_{[\alpha_1,\alpha_2,\ldots]}}{\partial \alpha_i} = 0, \tag{310}$$

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.

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Exercise:

(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 $\alpha \geq 0$. 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 $\epsilon = 2.3381$.

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12.2 Example: electron-electron repulsion

Ground state of Helium atom

As a trial function for the He ground a good ansatz could be a simple product of wave functions,

$$\psi_T(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{\alpha^3}{\pi\, a_0^3}\, e^{-\alpha\, r_1/a_0}\, e^{-\alpha\, r_2/a_0}. \tag{311}$$

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

$$\langle\psi_T| -\frac{\hbar^2}{2m}\left(\boldsymbol{\nabla}_1^2 + \boldsymbol{\nabla}_2^2\right)|\psi_T\rangle = \frac{\hbar^2}{m\, a_0^2}\,\alpha^2 = 2\,\alpha^2\, R_\infty, \tag{312}$$

$$\langle\psi_T|\frac{-Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)|\psi_T\rangle = -\frac{2Ze^2}{4\pi\epsilon_0\, a_0}\,\alpha = -4\,Z\alpha\, R_\infty, \tag{313}$$

$$\langle\psi_T|\frac{e^2}{4\pi\epsilon_0\, r_{12}}|\psi_T\rangle = \frac{5}{4}\,\alpha\, R_\infty, \tag{314}$$

and thus

$$E_{[\alpha]} = 2\left[\alpha^2 - \left(2Z - \frac{5}{8}\right)\alpha\right] R_\infty, \tag{315}$$

which is minimized for

$$\alpha = Z_{\rm eff} = Z - \frac{5}{16} \tag{316}$$

with

$$E[\alpha_{\rm min}] = -2\left(Z - \frac{5}{16}\right)^2 R_\infty. \tag{317}$$

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 value using perturbation theory (which of course is just the result obtained for $\alpha = 2$). As expected the value $Z_{\rm eff} = 27/16$ is less than 2.

The H^--ion

An interesting second example is actually the hydrogen atom, which also has a positive electron affinity, $H + e^- \rightarrow H^- + 0.76$ eV. Here, adding a second electron actually is harder to deal with in a variational approach. If one tries for the two electrons in H^- a simple product wave function does not produce a positive electron affinity (check this). 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

$$\psi_T = C\left[e^{-(\alpha_1 r_1 + \alpha_2 r_2)/a_0} + e^{-(\alpha_1 r_2 + \alpha_2 r_1)/a_0}\right]. \tag{318}$$

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.

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Exercise: Apply the variational principle to find a suitable wave function for H^-. Try the product wave function 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

$$\int d^3r_1\, d^3r_2\, \frac{e^{-2\alpha_1 r_1 - 2\alpha_2 r_2}}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \left(\frac{\pi}{\alpha_1^3}\right)\left(\frac{\pi}{\alpha_2^3}\right) \frac{\alpha_1\alpha_2\,\left(\alpha_1^2 + \alpha_2^2 + 3\,\alpha_1\alpha_2\right)}{(\alpha_1+\alpha_2)^3} \stackrel{\alpha_1=\alpha_2}{=} \frac{5}{8}\,\alpha\,\left(\frac{\pi}{\alpha^3}\right)^2 .$$

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12.3 The Hartree-Fock model

The Hartree-Fock model is a self-consistent model for determining the effective potential for electrons that we discussed earlier in the context of the periodic table. It starts from the Hamiltonian like in Eq. 251 including all electron-electron interactions, The variational approach is actually done through a self-consistent solution of

$$\delta\langle\psi|H - E|\psi\rangle = 0, \tag{319}$$

under varying the solution ψ, restricting oneself to solutions in the form of an antisymmetrized product (Slater determinant) of (normalized) single electron wave functions,

$$\psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_Z) = \mathcal{A}\phi_1(\boldsymbol{r}_1)\ldots\phi_Z(\boldsymbol{r}_Z), \tag{320}$$

which satisfy

$$\left[\frac{\hbar^2}{2m}\,\boldsymbol{\nabla}_i^2 - \frac{Z\,e^2}{4\pi\epsilon_0\,r_i} + \underbrace{\sum_{j\neq i}\int d^3r_j\;|\phi_j(\boldsymbol{r}_j)|^2\,\frac{e^2}{4\pi\epsilon_0\,|\boldsymbol{r}_i - \boldsymbol{r}_j|}}_{W_i(\boldsymbol{r}_i)} - E_i\right]\phi_i(\boldsymbol{r}_i) = 0 \tag{321}$$

The solution can be obtained iteratively by starting with an ansatz for the potential $W_i(\boldsymbol{r}_i)$, solve for the single particle solutions, reconstruct the new $W_i(\boldsymbol{r}_i)$, continuing till convergence is reached for the effective potential W.

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Exercise: Start for Helium with $W_i(\boldsymbol{r}_i) = 0$ and construct the potential $W_i(\boldsymbol{r}_i)$ after one step and look if you can find $Z_{\rm eff}(r)$ as in Eq. 252.

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13 Time-dependent perturbation theory

13.1 Explicit time-dependence

Repeating the case of a hamiltonian without explicit time-dependence, i.e. $H_0 = H_0(\boldsymbol{r}, \boldsymbol{p}, \ldots)$. One employs the time-independent solutions of the eigenvalue equation $H(\boldsymbol{r}, \boldsymbol{p}, \ldots)\phi_n = E_n\,\phi_n$. Using the completeness of the states ϕ_n one can write

$$\psi(t) = \sum_n c_n(t)\phi_n, \tag{322}$$

insert this in the Schrödinger equation,

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi(t) \tag{323}$$

leading to

$$i\hbar\dot{c}_n(t) = E_n\,c_n(t) \quad \Longrightarrow \quad c_n(t) = c_n\,e^{-i\,E_n t/\hbar}, \tag{324}$$

with constant coefficients $c_n = c_n(0)$. There are two possibilities:

1. One starts (e.g. after a measurement) with $\psi(0) = \phi_i$, where ϕ_i is *one* of the eigenstates of H_0 with eigenvalue/energy E_i. In that case
$$\psi(t) = \phi_i\,e^{-iE_i t/\hbar}, \tag{325}$$
known as a *stationary* state. All expectation values of operators (that do not explicitly depend on time) are time-independent.

2. One starts in a mixed state, say $\psi(0) = c_1\,\phi_1 + c_2\,\phi_2$. In that case one has
$$\psi(t) = c_1\,\phi_1\,e^{-iE_1 t/\hbar} + c_2\,\phi_2\,e^{-iE_2 t/\hbar}, \tag{326}$$
which leads to oscillations in expectation values with frequency $\omega_{12} = (E_1 - E_2)/\hbar$.

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 $\phi_n\,e^{-iE_n t/\hbar}$. We consider the case that the time-dependence is contained in a part of the Hamiltonian.

$$H = H_0 + V(t). \tag{327}$$

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 ϕ_n and eigen-energies E_n. When doing time-independent perturbation theory (i.e. the case that V is time-independent) one tries to express the true eigenfunctions of H in the complete set ϕ_n. In the present treatment one makes the observation that if the system at some time is in a state ϕ_i, it will at a later time have a nonzero probability to be in another state. The calculation of the rate of change is what is done in time-dependent perturbation theory. This can actually be used for both time-independent and time-dependent perturbations.

Starting with the known (time-independent) part H_0, we use completeness of the states ϕ_n to write

$$\psi(t) = \sum_n c_n(t)\,\phi_n\,e^{-iE_n t/\hbar}. \tag{328}$$

Note that one could have absorbed the exponential time-dependence in $c_n(t)$, but not doing so is more appropriate because the time-dependence of c_n is then solely a consequence of V.

By substituting the expression for $\psi(t)$ in the Schrödinger equation,

$$i\hbar\,\frac{\partial}{\partial t}\psi(t) = (H_0 + V(t))\,\psi(t), \tag{329}$$

one simply finds

$$i\hbar\,\dot{c}_p(t) = \sum_n V_{pn}(t)\,c_n(t)\,e^{+i\,\omega_{pn}t}, \tag{330}$$

where $V_{pn} = \langle\phi_p|V(t)|\phi_n\rangle$ is the expectation value of the potential V between the (time-independent) eigenstates of H_0, and $\omega_{pn} = (E_p - E_n)/\hbar$. As expected if $V = 0$, 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. Often, however, one will encounter a perturbative approach treated after that example.

13.2 Example: two-level system

Consider a two-state system, with ϕ_a and ϕ_b being solutions of the unperturbed Hamiltonian with eigenvalues E_a and E_b, $H_0\,\phi_a = E_a\,\phi_a$ and $H_0\,\phi_b = E_b\,\phi_b$. Using a matrix notation and the basis

$$\phi_a \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \phi_b = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{331}$$

the Hamiltonian H_0 and the perturbation V are taken to be

$$H_0 = \begin{pmatrix} E_a & 0 \\ 0 & E_b \end{pmatrix} \quad \text{and} \quad V = \begin{pmatrix} V_{aa}(t) & V_{ab}(t) \\ V_{ba}(t) & V_{bb}(t) \end{pmatrix} = \begin{pmatrix} 0 & V_{ab}(t) \\ V^*_{ab}(t) & 0 \end{pmatrix}. \tag{332}$$

We have restrict ourselves to the simpler situation that there is only a time-dependent off-diagonal element. Most applications can be cast in this form anyway. The solution can be written as

$$\psi(t) = c_a(t) \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-iE_at/\hbar} + c_b(t) \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{-iE_bt/\hbar} = \begin{pmatrix} c_a(t)\,e^{-iE_at/\hbar} \\ c_b(t)\,e^{-iE_bt/\hbar} \end{pmatrix}, \tag{333}$$

and the coefficients $c_a(t)$ and $c_b(t)$ obey a simple coupled set of equations of the form

$$\begin{aligned} i\hbar \begin{pmatrix} \dot{c}_a(t) \\ \dot{c}_b(t) \end{pmatrix} &= \begin{pmatrix} 0 & V_{ab}(t)\,e^{+i\omega_{ab}t} \\ V^*_{ab}(t)\,e^{-i\omega_{ab}t} & 0 \end{pmatrix} \begin{pmatrix} c_a(t) \\ c_b(t) \end{pmatrix} \\ &\equiv \hbar \begin{pmatrix} 0 & v(t) \\ v^*(t) & 0 \end{pmatrix} \begin{pmatrix} c_a(t) \\ c_b(t) \end{pmatrix}, \end{aligned} \tag{334}$$

representing simple coupled equations,

$$i\,\dot{c}_a(t) = v(t)\,c_b(t), \tag{335}$$

$$i\,\dot{c}_b(t) = v^*(t)\,c_a(t), \tag{336}$$

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Exercise: Show that in the presence of $V_{aa}(t) \equiv \hbar v_a(t)$ and $V_{bb}(t) \equiv \hbar v_b(t)$ in the two-channel case one can get again a 'simple' coupling problem if we start with the ansatz

$$\psi(t) = \begin{pmatrix} c_a(t)\,e^{-iE_at/\hbar}\,e^{-i\int_0^t dt'\ v_a(t')} \\ c_b(t)\,e^{-iE_bt/\hbar}\,e^{-i\int_0^t dt'\ v_b(t')} \end{pmatrix},$$

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Two-level system with harmonic perturbation

Let us assume a harmonic time dependence for $V_{ab}(t)$. An example would be the following hamiltonian for a two-state system,

$$H = -\boldsymbol{\mu} \cdot \boldsymbol{B}(t) = -\gamma\, \boldsymbol{s} \cdot \boldsymbol{B}(t), \tag{337}$$

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. Starting with a constant magnetic field in (say) the z-direction, $\boldsymbol{B}_0 = (0, 0, B_0)$, and using the matrix representation for a spin 1/2 particle one has

$$H_0 = -\frac{\gamma B_0}{2}\, \hbar\, \sigma_z = -\frac{\gamma B_0}{2}\, \hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{338}$$

The solutions are easily obtained,

$$\phi_a = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{with} \quad E_a = -\frac{\gamma B_0}{2}\, \hbar, \tag{339}$$

$$\phi_b = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{with} \quad E_b = \frac{\gamma B_0}{2}\, \hbar, \tag{340}$$

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 $\omega_{ab} = (E_a - E_b)/\hbar = -\gamma\, B_0$, known as the *Larmor frequency.*

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

$$\begin{aligned} H &= -\frac{\gamma B_0}{2}\, \hbar\, \sigma_z - \frac{\gamma B_1}{2}\, \hbar(\sigma_x\, \cos\omega t + \sigma_y\, \sin\omega t) \\ &= -\frac{\gamma B_0}{2}\, \hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \frac{\gamma B_1}{2}\, \hbar \begin{pmatrix} 0 & e^{-i\omega t} \\ e^{+i\omega t} & 0 \end{pmatrix}. \end{aligned} \tag{341}$$

We thus have a harmonic perturbation of the form

$$V_{ab}(t) = -\frac{\gamma B_1}{2}\, e^{-i\omega t} \quad \text{and} \quad v(t) = \frac{V_{ab}(t)}{\hbar}\, e^{+i\omega_{ab} t} = v_1\, e^{-i(\omega - \omega_{ab})t}. \tag{342}$$

with $v_1 = -\gamma B_1/2$.

The coupled equations in Eq. 334 can now simply be rewritten into a second order differential equation for c_a,

$$\ddot{c}_a + i(\omega - \omega_{ab})\, \dot{c}_a + v_1^2\, c_a = 0. \tag{343}$$

This equation has two independent solutions of the form $e^{i\,pt}$ with

$$p = -\frac{1}{2}\, (\omega - \omega_{ab}) \pm \omega_r \tag{344}$$

with the *Rabi flopping frequency* $\omega_r = \frac{1}{2}\sqrt{(\omega - \omega_{ab})^2 + 4v_1^2}$. The general solution can then be written as

$$\begin{aligned} c_a(t) &= e^{-\frac{1}{2} i(\omega - \omega_{ab})t}\, (A\, \sin(\omega_r\, t) + B\, \cos(\omega_r\, t))\,, \\ c_b(t) &= \frac{i}{v(t)}\, \dot{c}_a(t). \end{aligned} \tag{345}$$

Starting off with $c_a(0) = 0$ and $|c_b(0)| = 1$, it is straightforward to check that

$$c_a(t) = A\, e^{-\frac{1}{2}\, i\, (\omega - \omega_{ab})t}\, \sin(\omega_r\, t), \tag{346}$$

$$|A|^2 = \frac{v_1^2}{\omega_r^2} = \frac{\gamma^2 B_1^2}{(\omega - \omega_{ab})^2 + \gamma^2 B_1^2}, \tag{347}$$

$$|c_a(t)|^2 + |c_b(t)|^2 = 1. \tag{348}$$

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 ω_r, while the magnitude depends on the frequency of the rotating perpendicular $\boldsymbol{B}_1$ field, showing a resonance at $\omega = \omega_{ab}$. In that case the spin completely flips from parallel to antiparallel and back with frequency ω_r (at resonance we have $\omega_r = |v_1|$).

13.3 Fermi's golden rule

In many case we are not able to exactly solve the time-dependent problem and we treat the problem perturbatively. Writing, $H = H_0 + \lambda\, V(t)$, including a multiplicative factor λ to keep track of orders. In the case of perturbation theory, we realize that in writing a solution of the form

$$c_p(t) = c_p^{(0)}(t) + \lambda\, c_p^{(1)}(t) + \ldots, \tag{349}$$

the time-dependence of a specific order is determined by the next lower order,

$$i\hbar\, \dot{c}_p^{(m+1)} = \sum_n V_{pn}(t)\, c_n^{(m)}(t)\, e^{+i\,\omega_{pn} t}. \tag{350}$$

Starting with $c_p(0) = \delta_{pi}$, one immediately sees that the first two orders are given by

$$c_p^{(0)}(\tau) = \delta_{pi}, \tag{351}$$

$$c_p^{(1)}(\tau) = \frac{1}{i\hbar} \int_0^\tau dt\; V_{pi}(t)\, e^{+i\,\omega_{pi} t}. \tag{352}$$

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 ϕ_p, which means the probability for a transition $i \to p$. The first order result is valid if $|c_p^{(0)}(\tau) + c_p^{(1)}(\tau)|^2 \approx 1$.

Even 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. For a time-independent interactions V, and slightly more general for an interaction with a harmonic time dependence proportional to $e^{-i\,\omega t}$, we can easily obtain the coefficient $c_p^{(1)}$. If V is sufficiently weak, we find the result in first order perturbation theory,

$$\begin{aligned} c_p^{(1)}(\tau) &= \frac{|V_{pi}|}{i\hbar} \int_0^\tau dt\; e^{-i(\omega - \omega_{pi})t} = \frac{|V_{pi}|}{\hbar(\omega - \omega_{pi})}\, e^{-i(\omega - \omega_{pi})t}\Big|_0^\tau \\ &= \frac{|V_{pi}|}{\hbar(\omega - \omega_{pi})} \left(1 - e^{-i(\omega - \omega_{pi})\tau}\right) = \frac{2\,|V_{pi}|}{\hbar(\omega - \omega_{pi})}\, \sin((\omega - \omega_{pi})\tau/2)\, e^{-i\,(\omega - \omega_{pi})\tau/2}, \end{aligned} \tag{353}$$

and thus for $p \neq i$,

$$P_{i\to p}^{(1)}(\tau) = \frac{4\,|V_{pi}|^2}{\hbar^2}\, \frac{\sin^2((\omega - \omega_{pi})\tau/2)}{(\omega - \omega_{pi})^2}. \tag{354}$$

The function

$$f(\omega) = \frac{\sin^2(\omega\tau/2)}{\omega^2}$$

is for increasing times τ ever more strongly peaked around $\omega = 0$. The value at zero is $f(0) = \tau^2/4$, the first zeros are at $|\omega| = 2\pi/\tau$. Since

$$\int d\omega \; \frac{\sin^2(\omega\tau/2)}{\omega^2} = \frac{\pi\,\tau}{2}, \tag{355}$$

we approximate

$$\frac{\sin^2(\omega\tau/2)}{\omega^2} = \frac{\pi\,\tau}{2}\,\delta(\omega). \tag{356}$$

Then we find[5]

$$P^{(1)}_{i\to p}(\tau) = \tau\,\frac{2\pi}{\hbar}\,|V_{pi}|^2\,\delta(E_p - E_i - Q) \tag{357}$$

where $Q = \hbar\omega$, or for the transition probability per unit time,

$$W_{i\to p} \approx \dot{P}^{(1)}_{i\to p} = \frac{2\pi}{\hbar}\,|V_{pi}|^2\,\delta(E_p - E_i - Q) \qquad \text{Fermi's Golden Rule.} \tag{358}$$

Including a harmonic perturbation, Fermi's golden rule implies $E_f = E_i + Q$, where Q is the energy transferred to the system in the interaction. 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* $\rho_f(E)$, where $\rho_f(E)\,dE$ is the number of states in an energy interval dE around E. The transition probability per unit time is then given by

$$W_{i\to f} \approx \int dE_p\,\rho_f(E_p)\,\frac{2\pi}{\hbar}\,|V_{fi}|^2\,\delta(E_p - E_i - Q) = \frac{2\pi}{\hbar}\,|V_{fi}|^2\,\rho_f(E_i + Q) \tag{359}$$

(Fermi's Golden Rule No. 2).

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Exercise: The cross section $d\sigma$ in scattering theory is defined as the ratio between number of particles scattered under a particular angle divided by the flux of incoming particles

$$n(\theta,\varphi)\,d\Omega = |\boldsymbol{j}_i|\,d\sigma(\theta,\varphi),$$

The left hand side is given by $W_{i\to f} = W_{p\to p'}$, which is the transition probability per unit time of a plane wave $\phi_i = \phi_p$ into a plane wave $\phi_f = \phi_{p'}$, for which we use Fermi's Golden Rule.

(a) Calculate for a plane wave $\phi_i(\boldsymbol{r}) = \phi_p(\boldsymbol{r}) = \sqrt{\rho}\,\exp(i\boldsymbol{p}\cdot\boldsymbol{r})$ the flux $|\boldsymbol{j}_i|$.

(b) Calculate the density of states in the final state,

$$\rho_f(E')\,dE'\,d\Omega = \frac{1}{\rho}\,\frac{d^3p'}{(2\pi\hbar)^3}.$$

(c) Show that the matrix element V_{fi} is proportional to the Fourier transform of $V(\boldsymbol{r})$,

$$V_{fi} = \rho\int d^3r\; V(\boldsymbol{r})\,\exp(i\,\boldsymbol{q}\cdot r) = \rho\,\tilde{V}(\boldsymbol{q}).$$

Express $\boldsymbol{q}$ in $\boldsymbol{p}$ and $\boldsymbol{p}'$.

(d) Combine all results to find $d\sigma/d\Omega$.

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[5] $\delta(ax) = \frac{1}{|a|}\,\delta(x)$

14 Emission and absorption of radiation and lifetimes

14.1 Application: emission and absorption of radiation by atoms

We take a plane wave for the scalar and vector potential,

$$\phi = \tilde{\phi}(\boldsymbol{k},\omega)\, \exp[i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)], \tag{360}$$

$$\boldsymbol{A} = \tilde{\boldsymbol{A}}(\boldsymbol{k},\omega)\, \exp[i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)], \tag{361}$$

with $\omega = |\boldsymbol{k}|c$, corresponding with the energy and momentum relation, $E = |\boldsymbol{p}|c$, for a massless photon. Although the physical fields are real, we can work with the plane waves by always taking also the complex conjugate solution into account. The corresponding behavior for the electric and magnetic fields can be obtained from the potentials[6]

$$\boldsymbol{E} = \tilde{\boldsymbol{E}}(\boldsymbol{k},\omega)\, \exp[i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)], \tag{362}$$

$$\boldsymbol{B} = \tilde{\boldsymbol{B}}(\boldsymbol{k},\omega)\, \exp[i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)]. \tag{363}$$

The interaction of matter with an electromagnetic field is given by

$$H_{int} = \int d^3r\ \left[\rho(\boldsymbol{r})\,\phi(\boldsymbol{r}) - \boldsymbol{j}(\boldsymbol{r})\cdot\boldsymbol{A}(\boldsymbol{r})\right], \tag{364}$$

where ρ and $\boldsymbol{j}$ are the charge and current distribution. The dipole approximation is valid when the wave length $\lambda = 2\pi/|\boldsymbol{k}|$ is much larger than the typical size of the system, e.g. for light ($\lambda \approx 6000$ Å) and atoms (size $\approx 1 - 10$ Å). In that case one can restrict oneself to the first nontrivial term in

$$\exp[i(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t)] = e^{-i\,\omega t}\,(1 + i\,\boldsymbol{k}\cdot\boldsymbol{r} + \ldots). \tag{365}$$

One obtains

$$H_{int} = e^{-i\omega t}\int d^3r\ \left[(1 + i\,\boldsymbol{k}\cdot\boldsymbol{r})\,\rho(\boldsymbol{r})\,\tilde{\phi}(\boldsymbol{k},\omega) - (1 + i\,\boldsymbol{k}\cdot\boldsymbol{r})\,\boldsymbol{j}(\boldsymbol{r})\cdot\tilde{\boldsymbol{A}}(\boldsymbol{k},\omega)\right] \tag{366}$$

$$= e^{-i\omega t}\left[Q\,\tilde{\phi}(\boldsymbol{k},\omega) - \boldsymbol{D}\cdot\tilde{\boldsymbol{E}}(\boldsymbol{k},\omega) - \boldsymbol{\mu}\cdot\tilde{\boldsymbol{B}}(\boldsymbol{k},\omega) + \ldots\right], \tag{367}$$

where we have used that $i\,\boldsymbol{k}\,\tilde{\phi} = -\tilde{\boldsymbol{E}} + (\omega/c)\,\tilde{\boldsymbol{A}}$ and $i\,\boldsymbol{k}\times\tilde{\boldsymbol{A}} = \tilde{\boldsymbol{B}}$. The charge and current distributions give rise to charge, electric and magnetic dipole moments,

$$Q = \int d^3r\ \rho(\boldsymbol{r}) \Longrightarrow \sum_i q_i, \tag{368}$$

$$\boldsymbol{D} = \int d^3r\ \boldsymbol{r}\,\rho(\boldsymbol{r}) \Longrightarrow \sum_i q_i\,\boldsymbol{r}_i, \tag{369}$$

$$\boldsymbol{\mu} = \int d^3r\ \boldsymbol{r}\times\boldsymbol{j}(\boldsymbol{r}) \Longrightarrow \sum_i \frac{q_i}{m_i}\,\boldsymbol{\ell}_i, \tag{370}$$

The results after the arrow in the above equations 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 ($\boldsymbol{D}$).

[6] Recall that

$$\boldsymbol{E} = -\boldsymbol{\nabla}\Phi - \frac{1}{c}\,\frac{\partial\boldsymbol{A}}{\partial t},$$
$$\boldsymbol{B} = \boldsymbol{\nabla}\times\boldsymbol{A}$$

The radiation fields can be obtained from the vector potential

$$\boldsymbol{A} = \boldsymbol{\epsilon}(\boldsymbol{k},\omega)\,\frac{c\,\tilde{E}_0(\boldsymbol{k},\omega)}{i\,\omega}\,\exp[i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)] \tag{371}$$

and $\phi = 0$. The vector $\boldsymbol{\epsilon}$ is called the polarization. One has

$$\boldsymbol{E} = \boldsymbol{\epsilon}\,\tilde{E}_0\,\exp[i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)], \tag{372}$$

$$\boldsymbol{B} = \frac{\boldsymbol{k}\times\boldsymbol{\epsilon}}{|\boldsymbol{k}|}\,\tilde{E}_0\,\exp[i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)]. \tag{373}$$

In the dipole approximation the interaction with matter is given by

$$V(t) = -\boldsymbol{D}\cdot\boldsymbol{E}(t) = -\boldsymbol{D}\cdot\boldsymbol{\epsilon}\,\tilde{E}_0\,e^{-i\,\omega t}. \tag{374}$$

We already calculated for such a time-dependent interaction, the transition amplitude,

$$c_p^{(1)}(\tau) = \frac{\langle\phi_p|\boldsymbol{D}\cdot\boldsymbol{\epsilon}|\phi_i\rangle\,E_0}{i\hbar}\;\frac{e^{i\,(\omega_{pi}-\omega)\tau}-1}{i\,(\omega_{pi}-\omega)}, \tag{375}$$

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

$$P_{i\to p}^{(1)}(\tau) = \frac{E_0^2(\omega)}{\hbar^2}\,|\langle\phi_p|\boldsymbol{D}\cdot\boldsymbol{\epsilon}|\phi_i\rangle|^2\,\frac{\pi\,\tau}{2}\,\delta(\omega-|\omega_{pi}|). \tag{376}$$

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 $d\omega$,

$$\frac{1}{2}\,\epsilon_0\,E_0^2(\omega)\,d\omega = \frac{N(\omega)\,\hbar\omega}{c}\,d\omega. \tag{377}$$

Integrating over the photon frequencies, one sees that the atom absorps or emits photons of the right frequency leading to a transition rate

$$\dot{P}_{i\to p}^{(1)} = \frac{\pi}{\epsilon_0\,\hbar c}\,|\omega_{pi}|\,N(|\omega_{pi}|)\,|\langle\phi_p|\boldsymbol{D}\cdot\boldsymbol{\epsilon}|\phi_i\rangle|^2. \tag{378}$$

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

$$W_{i\to p} = \overline{\dot{P}_{i\to p}^{(1)}} = \frac{4}{3}\,\pi^2\,\alpha\,|\omega_{pi}|\,N(|\omega_{pi}|)\,|\langle\phi_p|\boldsymbol{R}|\phi_i\rangle|^2. \tag{379}$$

Note that by treating also the electromagnetic field quantummechanically one finds in addition to the *stimulated absorption or emission* rate a *spontaneous emission* rate

$$W_{i\to p}^{\text{spont.}} = \frac{4}{3}\,\alpha\,\frac{\omega_{ip}^3}{c^2}\,|\langle\phi_p|\boldsymbol{R}|\phi_i\rangle|^2, \tag{380}$$

governed by the same transition matrix element and thus obeying the same selection rules.

14.2 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

$$P(t) = P(0)\,e^{-\gamma\,t} = P(0)\,e^{-t/T}, \tag{381}$$

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

$$|\psi_n(t)\rangle \propto e^{-i\,E_n t/\hbar - \gamma_n t/2}. \tag{382}$$

We can expand a decaying state in eigenmodes according to

$$e^{-i\,E_n t/\hbar - \gamma_n t/2}\,\theta(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\,c(\omega)\,e^{-i\,\omega t}, \tag{383}$$

(including the Heavyside step function θ) with

$$\begin{aligned} c(\omega) &= \int_0^\infty dt\; e^{+i\,(\omega-\omega_n+i\gamma_n/2)t} \\ &= \frac{-i}{\omega-\omega_n+i\gamma_n/2} e^{+i\,(\omega-\omega_n+i\gamma_n/2)t}\Big|_0^\infty \\ &= \frac{i}{\omega-\omega_n+i\gamma_n/2}. \end{aligned} \tag{384}$$

For unstable states the transition amplitude for emission or absorption of a photon is then proportional to

$$\begin{aligned} T(\omega) &= \int \frac{d\omega_1'}{2\pi}\,\frac{d\omega_2'}{2\pi}\,c_2^*(\omega_2')\,c_1(\omega_1')\,2\pi\,\delta(\omega-\omega_1'+\omega_2') \\ &= \int \frac{d\omega'}{2\pi} c_2^*(\omega')\,c_1(\omega'+\omega) \\ &= \int \frac{d\omega'}{2\pi} \int_0^\infty dt_1 \int_0^\infty dt_2\; e^{-i\,(\omega'-\omega_2-i\gamma_2/2)t_2}\,e^{+i\,(\omega'+\omega-\omega_1+i\gamma_1/2)t_1} \\ &= \int_0^\infty dt_1 \int_0^\infty dt_2\; e^{+i\,(\omega_2+i\gamma_2/2)t_2}\,e^{+i\,(\omega-\omega_1+i\gamma_1/2)t_1}\,\delta(t_1-t_2) \\ &= \int_0^\infty dt\; e^{+i\,(\omega-\omega_{12}+i\gamma_{12}/2)t} = \frac{i}{\omega-\omega_{12}+i\gamma_{12}/2}, \end{aligned} \tag{385}$$

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

$$I(\omega) = I_0\,\frac{\Gamma_{12}^2/4}{\hbar^2\,(\omega-\omega_{12})^2 + \Gamma_{12}^2/4}, \tag{386}$$

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.

15 Adiabatic processes

15.1 Sudden and adiabatic approximation

The *sudden approximation*, where an instantaneous jump between (time-independent) Hamiltonians H_- and H_+ at time $t = 0$ is considered, in essence involves reexpressing the instantaneous wave function $\psi(0)$ in terms of the new eigenstates of H_+, which determines the time evolution for $t > 0$. Its validity can be investigated and requires the timescale of the change to be much faster than the typical timescales related to the initial motion.

The opposite is an adiabatic approximation, where the change in the Hamiltonian is slow. Although the treatment is similar on some parts, the difference with time-dependent perturbation theory is that the whole system (full spectrum) changes, usually due to the environment, expressed as $H(t) = H(\boldsymbol{R}(t))$. One might think here of moving the center of mass of a complex system through an environment that determines (part of) the Hamiltonian, but also of changing gradually some other external parameters, such as slowly increasing the strength of a confining harmonic oscillator well or of slowly varying electric or magnetic fields.

We simply start with writing down instantaneous sets of (normalized) eigenfunctions,

$$H(t)\phi_n(t) = E_n(t)\,\phi_n(t), \tag{387}$$

and solve for

$$i\hbar\,\frac{\partial}{\partial t}\psi = H(t)\,\psi(t). \tag{388}$$

For the solution we use the ansatz

$$\psi(t) = \sum_n c_n(t)\,\phi_n(t)\,e^{i\theta_n(t)}, \tag{389}$$

with

$$i\theta_n(t) = \frac{1}{i\hbar}\int_0^t dt'\; E_n(t'), \tag{390}$$

satisfying $i\dot{\theta}_n(t) = E_n(t)/i\hbar = -i\,\omega_n(t)$. Singling out this phase is just convenient, generalizing the time-independent treatment. For a time-independent Hamiltonian with time-independent eigenfunctions and eigenvalues we actually get $i\theta_n(t) = -i\omega_n t$.

We find from the Schrödinger equation that

$$\dot{c}_p = -\sum_n \langle\phi_p|\dot{\phi}_n\rangle\,c_n\,e^{i(\theta_n-\theta_p)}. \tag{391}$$

Note all quantities in this expression are time-dependent. The matrix element can be related to the matrix element of $\dot{H}$, starting from Eq. 387, $\dot{H}\phi_n = -H\dot{\phi}_n + E_n\dot{\phi}_n + \dot{E}_n\phi_n$, giving

$$\langle\phi_p|\dot{H}|\phi_n\rangle = (E_n - E_p)\,\langle\phi_p|\dot{\phi}_n\rangle. \tag{392}$$

This gives the result

$$\dot{c}_p = -\langle\phi_p|\dot{\phi}_p\rangle\,c_p - \sum_{n\neq p}\frac{\langle\phi_p|\dot{H}|\phi_n\rangle}{E_n - E_p}\,c_n\,e^{i(\theta_n-\theta_p)}. \tag{393}$$

In the *adiabatic limit* the change of the Hamiltonian is assumed to be small compared to the intrinsic time-dependence, which is of the order of $\hbar/\Delta E$, where ΔE are typical energies or energy differences in the spectrum. Therefore, omitting the second term, and starting with $\psi(0) = \phi_n(0)$ in the nth eigenstate, one gets in the adiabatic limit

$$\psi(t) = e^{i\theta_n(t)}\,e^{i\gamma_n(t)}\,\phi_n(t), \tag{394}$$

where the phase γ_n, defined as

$$\gamma_n(t) \equiv i \int_0^t dt' \ \langle \phi_n | \dot{\phi}_n \rangle, \tag{395}$$

incorparates the effect of the (first) term on the righthandside in Eq. 393. As defined, the phase γ_n is real, because it's imaginary part (the real part of $\langle \phi_n | \dot{\phi}_n \rangle$) is zero for normalized wave functions. The phase γ_n is known as *Berry's phase*.

15.2 An example: Berry's phase for an electron in a precessing field

For an electron in a precessing magnetic field one has (using $\omega_0 = -\gamma\, B$),

$$\begin{aligned} H(t) &= -\gamma\, \boldsymbol{S} \cdot \boldsymbol{B} = \frac{\hbar\omega_0}{2} \left(\cos\alpha\, \sigma_z + \sin\alpha\, \cos(\omega t)\, \sigma_x + \sin\alpha\, \sin(\omega t)\, \sigma_y \right) \\ &= \frac{\hbar\omega_0}{2} \begin{pmatrix} \cos\alpha & e^{-i\omega t}\, \sin\alpha \\ e^{+i\omega t}\, \sin\alpha & -\cos\alpha \end{pmatrix}. \end{aligned}$$

The energies are $E_\pm = \pm\hbar\omega_0/2$ and the normalized eigenspinors are

$$\chi_+(t) = \begin{pmatrix} \cos(\alpha/2)\, e^{-i\omega t/2} \\ \sin(\alpha/2)\, e^{+i\omega t/2} \end{pmatrix}, \qquad \chi_-(t) = \begin{pmatrix} -\sin(\alpha/2)\, e^{-i\omega t/2} \\ \cos(\alpha/2)\, e^{+i\omega t/2} \end{pmatrix}.$$

In this case the exact solution is actually known (see Eq. 346). With the appropriate starting point and realizing that in this case the Rabi frequency is

$$\omega_r = \tfrac{1}{2} \sqrt{(\omega - \omega_0\, \cos\alpha)^2 + \omega_0^2\, \sin^2\alpha} = \tfrac{1}{2} \sqrt{\omega^2 + \omega_0^2 - 2\,\omega\omega_0\, \cos\alpha},$$

one has

$$\chi(t) = \begin{pmatrix} \cos(\alpha/2)\, e^{-i\omega t/2} \left(\cos(\omega_r t) - i\, \frac{(\omega_0 - \omega)}{2\,\omega_r}\, \sin(\omega_r t) \right) \\ \sin(\alpha/2)\, e^{+i\omega t/2} \left(\cos(\omega_r t) - i\, \frac{(\omega_0 + \omega)}{2\,\omega_r}\, \sin(\omega_r t) \right) \end{pmatrix}. \tag{396}$$

The overlap with $\chi_-(t)$ is (exactly)

$$|\langle \chi_-(t) | \chi(t) \rangle|^2 = \frac{\omega^2}{\omega_r^2}\, \sin^2\alpha\, \sin^2(\omega_r t).$$

In the adiabatic limit (ω small) the Rabi frequency becomes

$$\omega_r \approx \frac{1}{2} \left(\omega_0 - \omega\, \cos\alpha \right),$$

and one has $\omega \ll \omega_0 \sim \omega_r$. The overlap with $\chi_-(t)$ disappears and the remaining part is

$$\chi(t) \approx e^{-i\,\omega_0 t/2}\, e^{i(\omega\, \cos\alpha) t/2}\, \chi_+(t). \tag{397}$$

Using

$$i\, \dot{\chi}_+(t) = \tfrac{1}{2}\omega \begin{pmatrix} \cos(\alpha/2)\, e^{-i\omega t/2} \\ -\sin(\alpha/2)\, e^{+i\omega t/2} \end{pmatrix},$$

Berry's phase is indeed also found from Eq. 395

$$\gamma_+(t) = i \int_0^t dt' \ \langle \chi_+ | \dot{\chi}_+ \rangle = \tfrac{1}{2}\, (\omega\, \cos\alpha) t.$$

15.3 The geometric nature of Berry's phase

Berry's phase is an example of a phase that depends on the nature of solutions and their dependence on parameters, such as shape of potential, position in external fields. Such positions or shapes can return to their original position but still the phase may persist. The phase, however, does not depend on the time it takes to get back to the original situation, but on the path in the parameter space. Such a phase is called a *geometric phase*. To see the geometric nature of Berry's phase, one realizes that the time dependence in ϕ_n comes from the 'environment', summarized as the motion $\boldsymbol{R}(t)$ in parameter space. The change in $\phi_n(t) = \phi_n(\boldsymbol{R}(t)$ becomes

$$\dot{\phi}_n = \boldsymbol{\nabla}_R \, \phi_n \left(\boldsymbol{R}(t) \right) \cdot \frac{d\boldsymbol{R}}{dt},$$

and the phase is given by

$$\gamma_n(t) = i \int_0^t dt' \, \frac{d\boldsymbol{R}}{dt'} \cdot \langle \phi_n | \boldsymbol{\nabla}_R \, \phi_n \rangle = i \int_{\boldsymbol{R}_i}^{\boldsymbol{R}_f} d\boldsymbol{R} \cdot \langle \phi_n | \boldsymbol{\nabla}_R \, \phi_n \rangle. \tag{398}$$

For a closed contour C in $\boldsymbol{R}$-space, enclosing a surface S, this phase can also be written as a surface integral

$$\gamma_n(t) = i \oint_C d\boldsymbol{R} \cdot \langle \phi_n | \boldsymbol{\nabla}_R \, \phi_n \rangle = i \int_S d\boldsymbol{A} \cdot \boldsymbol{\nabla}_R \times \langle \phi_n | \boldsymbol{\nabla}_R \, \phi_n \rangle. \tag{399}$$

Example 1: Electron in rotating magnetic field

The example worked out in the previous section, can for the phase after a full cycle, also be done for the spinor corresponding to spin pointing in the direction (θ, φ).

$$\chi_+ = \begin{pmatrix} \cos(\theta/2) \\ e^{i\varphi} \, \sin(\theta/2) \end{pmatrix}.$$

(Note that this choice is well-defined at $\theta = 0$). Performing the calculation (use polar coordinates) one finds

$$\langle \chi_+ | \boldsymbol{\nabla} \chi_+ \rangle = i \, \frac{\sin^2(\theta/2)}{r \, \sin\theta} \, \hat{\boldsymbol{\varphi}}. \qquad \text{and} \qquad \boldsymbol{\nabla} \times \langle \chi_+ | \boldsymbol{\nabla} \chi_+ \rangle = \frac{i}{2\, r^2} \, \hat{\boldsymbol{r}}.$$

In one cycle of the magnetic field, the phase is

$$\gamma_+(\text{cycle}) = -\frac{1}{2} \int \frac{\hat{\boldsymbol{r}} \cdot d\boldsymbol{a}}{r^2} = -\frac{1}{2} \int d\Omega = -\frac{1}{2} \, \Omega, \tag{400}$$

where Ω is the solid angle swept out by the magnetic field, which is in the example of the electron in a rotating magnetic field was $\Omega = \pi(1 - \cos\alpha)$.

Example 2: the Bohm-Aharonov effect

Another famous example of a Berry type of phase is the phase acquired by an electron moving around a magnetic field enclosed in an infinitely long solenoid. In such a solenoid (radius R and taken along the z-axis) the $\boldsymbol{B}$-field is uniform inside the solenoid, it is zero outside and it is described by an electromagnetic vector potential

$$\begin{aligned} r < a: \qquad & \boldsymbol{A} = \frac{Br}{2} \, \hat{\boldsymbol{\varphi}} \;=\; \left(\frac{-By}{2}, \frac{Bx}{2}, 0 \right), \\ r > a: \qquad & \boldsymbol{A} = \frac{BR^2}{2\, r} \, \hat{\boldsymbol{\varphi}} = \; \left(\frac{-BR^2 \, y}{2\, r^2}, \frac{BR^2 \, x}{2\, r^2}, 0 \right). \end{aligned}$$

In quantum mechanics the field $\boldsymbol{A}$ is very relevant. In fact the Hamiltonian for a charge in an electromagnetic field is described by

$$H = \frac{1}{2m}\left(-i\hbar\boldsymbol{\nabla} - q\,\boldsymbol{A}\right)^2 + q\,\phi. \tag{401}$$

Taking the electric field zero, one sees that the solution is found by looking for eigenstates

$$(-i\hbar\boldsymbol{\nabla} - q\boldsymbol{A})\,\phi_k(\boldsymbol{r}) = \hbar\boldsymbol{k}\,\phi_k(\boldsymbol{r}). \tag{402}$$

Outside of the solenoid, where $\boldsymbol{\nabla}\times\boldsymbol{A} = 0$, the exact solutions involve a line integral

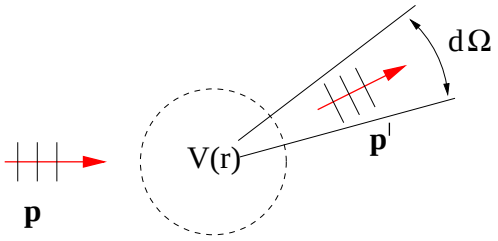
$$\phi_k(\boldsymbol{r};\boldsymbol{A}) = \exp\left(i\,\frac{q}{\hbar}\int_O^{\boldsymbol{r}} d\boldsymbol{s}\cdot A(\boldsymbol{s})\right)\,\exp\left(i\,\boldsymbol{k}\cdot\boldsymbol{r}\right). \tag{403}$$

This result is in fact nothing else than Berry's phase modifying the plane wave solution. Eq. 401 immediately gives us the gradient of $\phi_k(\boldsymbol{r})$, which can be used in Eq. 398 to get the phase.

16 Scattering theory

16.1 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,

$$n(\theta,\phi)\, d\Omega = |\boldsymbol{j}_{in}|\, d\sigma(\theta,\phi). \tag{404}$$

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.*

16.2 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, $\phi_i(\boldsymbol{r}) = \sqrt{\rho}\, \exp(i\, \boldsymbol{p} \cdot \boldsymbol{r}/\hbar)$, with energy $E = \boldsymbol{p}^2/2m$ and the detected final state, $\phi_f(\boldsymbol{r}) = \sqrt{\rho}\, \exp(i\, \boldsymbol{p}' \cdot \boldsymbol{r}/\hbar)$, 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),

$$n(\theta,\phi)\, d\Omega = \frac{2\pi}{\hbar} \left[|\langle \phi_f | V | \phi_i \rangle|^2\ \rho(E') \right]_{E'=E+Q}. \tag{405}$$

In order to get $d\sigma$ we need to get the flux $\mathscr{I}$ 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,
  $$\boldsymbol{j}(\boldsymbol{r},t) = \frac{\hbar}{2i\,m}\,(\psi^*\,\boldsymbol{\nabla}\psi - (\boldsymbol{\nabla}\psi)^*\psi) = \rho\,\frac{\boldsymbol{p}}{m} = \rho\,\boldsymbol{v}. \tag{406}$$
  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
  $$\rho(\boldsymbol{p})\,d^3p = \frac{1}{\rho}\,\frac{d^3p}{(2\pi\hbar)^3}. \tag{407}$$
  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,
  $$\mathbf{1} = \int d^3r\ |\boldsymbol{r}\rangle\,\langle\boldsymbol{r}| = \frac{1}{\rho}\int \frac{d^3p}{(2\pi\hbar)^3}\ |\boldsymbol{p}\rangle\,\langle\boldsymbol{p}|. \tag{408}$$
  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,
  $$\phi_p(\boldsymbol{r}) = \frac{1}{L^{3/2}}\,\exp(i\,\boldsymbol{p}\cdot\boldsymbol{r}/\hbar), \tag{409}$$
  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
  $$\rho(\boldsymbol{p}')d^3p' = \frac{1}{\rho}\,\frac{p'^2}{(2\pi\hbar)^3}\,dp'\,d\Omega' = \frac{1}{\rho}\,\frac{m\,p'}{(2\pi\hbar)^3}\,dE'\,d\Omega' = \rho(E')\,dE'\,d\Omega'. \tag{410}$$

With the flux and density of final states, we get immediately

$$d\sigma(\theta,\phi) = d\Omega'\left(\frac{m}{2\pi\hbar^2}\right)^2\,\frac{p'}{p}\,\left|\int d^3r\ \exp\left(\frac{i}{\hbar}\,(\boldsymbol{p}-\boldsymbol{p}')\cdot\boldsymbol{r}\right)\,V(\boldsymbol{r})\right|^2_{E'=E+Q}, \tag{411}$$

or introducing the Fourier transform

$$\tilde{V}(\boldsymbol{k}) = \int d^3r\ V(\boldsymbol{r})\,\exp(i\,\boldsymbol{k}\cdot r), \tag{412}$$

one obtains the following expression for the differential cross section in the socalled *Born approximation*,

$$\frac{d\sigma}{d\Omega'} = \left(\frac{m}{2\pi\hbar^2}\right)^2\,\frac{p'}{p}\,\left|\tilde{V}(\boldsymbol{q})\right|^2, \tag{413}$$

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*,

$$\sigma(E) = \int d\Omega\ \frac{d\sigma}{d\Omega}(E,\Omega). \tag{414}$$

Note that in the case of elastic scattering one has $p' = p$ in which case the momentum transfer squared is given by

$$\begin{aligned} \hbar^2 \boldsymbol{q}^2 &= |\boldsymbol{p} - \boldsymbol{p}'|^2 = p^2 + p'^2 + 2\,pp'\,\cos(\theta) \\ &= 2\,p^2(1-\cos\theta) = 4\,p^2\,\sin^2(\theta/2). \end{aligned} \tag{415}$$

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

$$\begin{aligned} \tilde{V}(\boldsymbol{q}) &= \int d^3r\; V(r)\,\exp(i\,\boldsymbol{q}\cdot\boldsymbol{r}) \\ &= 2\pi \int_0^\infty dr \int_{-1}^1 d\cos\alpha\; r^2 V(r)\, e^{i\,qr\,\cos\alpha} \\ &= \frac{4\pi}{q}\int_0^\infty dr\; rV(r)\,\sin(qr), \end{aligned} \tag{416}$$

only depends on $q = |\boldsymbol{q}|$.

==========

Exercise: 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 $\rho(E)$.

==========

16.3 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

$$\begin{aligned} \tilde{V}(\boldsymbol{q}) &= \frac{4\pi\,V_0}{q}\int_0^a dr\; r\,\sin(qr) \\ &= \frac{4\pi\,V_0}{q^3}\int_0^{qa} dx\; x\,\sin(x) \\ &= \frac{4\pi\,V_0}{q^3}\,[\sin qa - qa\,\cos qa] \\ &\overset{qa\ll 1}{\longrightarrow} \frac{4\pi\,V_0}{q^3}\left[qa - \frac{1}{3!}(qa)^3 - qa + \frac{1}{2!}(qa)^3 + \ldots\right] = \frac{4\pi}{3}\,V_0 a^3, \end{aligned} \tag{417}$$

leading for $E \to 0$ to

$$\frac{d\sigma}{d\Omega} \approx \frac{1}{9}\left(\frac{2m\,V_0\,a^2}{\hbar^2}\right)^2 a^2 \tag{418}$$

The Coulomb potential

The integral

$$\tilde{V}(\boldsymbol{q}) = -\frac{Ze^2}{4\pi\epsilon_0}\,\frac{4\pi}{q}\int_0^\infty dr\ \sin(qr) \tag{419}$$

diverges and we need to consider for instance the screened Coulomb potential, multiplied with $\exp(-\mu r)$. In that case one obtains

$$\begin{aligned}\tilde{V}(\boldsymbol{q}) &= -\frac{Ze^2}{4\pi\epsilon_0}\,\frac{4\pi}{q}\int_0^\infty dr\ \sin(qr)\,e^{-\mu r}\\ &= -\frac{Ze^2}{4\pi\epsilon_0}\,\frac{4\pi}{q}\int_0^\infty dr\ \frac{1}{2i}\left(e^{i(q+i\mu)r}-e^{i(q-i\mu)r}\right)\\ &= -\frac{Ze^2}{\epsilon_0}\,\frac{1}{q^2+\mu^2},\end{aligned} \tag{420}$$

allowing even the limit $\mu \to 0$ to be taken. Thus

$$\frac{d\sigma}{d\Omega}(E,\theta) = \left(\frac{m}{2\pi\,\hbar^2}\right)^2\left(\frac{Ze^2}{\epsilon_0}\right)^2\,\frac{1}{q^4} = \left(\frac{Ze^2}{8\pi\,\epsilon_0\,pv}\right)^2\,\frac{1}{\sin^4(\theta/2)}. \tag{421}$$

This result is known as the Rutherford cross section.

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Exercise: Derive the relativistic expression for the elastic Coulomb scattering cross section using the result of the exercise in the previous 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

$$\sigma(E)\ \propto\ \frac{p'}{p}\ =\ \sqrt{\frac{E'}{E}}. \tag{422}$$

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 $E \approx E_{\rm thr}$

$$\sigma(E)\ \propto\ \sqrt{E-E_{\rm thr}}. \tag{423}$$

For an exothermic process (with energy release $Q>0$) one can scatter for any (positive) energy E and one has near $E \approx 0$

$$\sigma(E)\ \propto\ \frac{1}{\sqrt{E}}. \tag{424}$$

Application to two-particle collisions

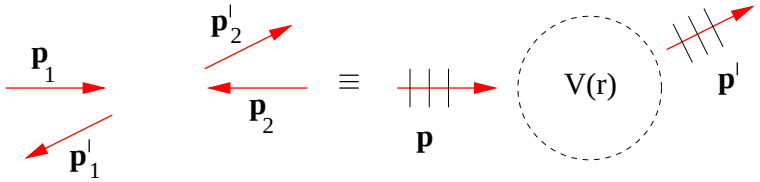
In most applications, the target is not an "external" potential, but rather two particles that collide (*collider experiments*) or one particle that is shot onto another one (*fixed target experiments*). This can in general lead to several possibilities corresponding to several *scattering channels*,

$$\begin{array}{lll} a+b \longrightarrow a+b & & \text{(elastic scattering)}\\ \left.\begin{array}{l}\longrightarrow\ c_1+c_2\\ \longrightarrow\ d_1+d_2+d_3\end{array}\right\} & & \text{(inelastic scattering)}\end{array} \tag{425}$$

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

$$\mathscr{I} = \rho \, |\boldsymbol{v}_1 - \boldsymbol{v}_2| = \rho \left| \frac{\boldsymbol{p}_1}{m_1} - \frac{\boldsymbol{p}_2}{m_2} \right| = \rho \left| \frac{\boldsymbol{p}}{\mu} \right|, \tag{426}$$

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.

17 Scattering off a composite system

17.1 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

$$H = H_{\rm system} + H_{\rm e} + V, \tag{427}$$

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

$$\begin{aligned} V(\boldsymbol{q}) &= \int d^3r \int d^3r'\ \exp(-i\,\boldsymbol{k}'\cdot\boldsymbol{r})\,\Phi_B^*(\boldsymbol{r}')\frac{-e^2}{4\pi\,\epsilon_0\,|\boldsymbol{r}-\boldsymbol{r}'|}\,\Phi_A(\boldsymbol{r}')\,exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) \\ &= -\frac{e^2}{4\pi\,\epsilon_0}\int d^3r\ \exp(i\,\boldsymbol{q}\cdot\boldsymbol{r})\int d^3r'\frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}, \end{aligned} \tag{428}$$

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

$$\begin{aligned} V(\boldsymbol{q}) &= -\frac{e^2}{4\pi\,\epsilon_0}\int d^3r'\ \exp(i\,\boldsymbol{q}\cdot\boldsymbol{r}')\int d^3r''\ \exp(i\,\boldsymbol{q}\cdot\boldsymbol{r}'')\,\frac{\rho(\boldsymbol{r}')}{r''} \\ &= -\frac{e^2}{4\pi\,\epsilon_0}\,\frac{4\pi}{q^2}\,F(\boldsymbol{q}), \end{aligned} \tag{429}$$

where we have introduced the form factor

$$F(\boldsymbol{q}) = \int d^3r\ \exp(i\,\boldsymbol{q}\cdot\boldsymbol{r})\,\rho(\boldsymbol{r}) \tag{430}$$

which is the Fourier transform of the density. The result for the cross section is

$$\frac{d\sigma}{d\Omega} = \left(\frac{m\,e^2}{2\pi\,\epsilon_0\,\hbar^2\,q^2}\right)^2\frac{p'}{p}\,|F(\boldsymbol{q})|^2\,. \tag{431}$$

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

$$\begin{aligned} \rho_{BA}(\boldsymbol{r}) &= \sum_{j=1}^{Z}\int\prod_{k=1}^{Z}d^3r_k\ \delta^3(\boldsymbol{r}-r_j)\,\Phi_B^*(r_1,\ldots,r_Z)\Phi_A(r_1,\ldots,r_Z) \\ &= Z\int\prod_{k=2}^{Z}\Phi_B^*(r,r_2,\ldots,r_Z)\Phi_A(r,r_2,\ldots,r_Z) = Z\,\rho_{BA}(\boldsymbol{r}). \end{aligned} \tag{432}$$

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 $Z^2|\delta_{ab} - F_{ba}|^2$.

17.2 Examples of form factors

Form factors as encountered in the previous section are defined as the Fourier transform of a density,

$$F(\boldsymbol{q}) = \int d^3r \ \exp(i\,\boldsymbol{q}\cdot\boldsymbol{r})\,\rho(\boldsymbol{r}). \tag{433}$$

As before in discussing the potential in momentum space, one has for a spherically symmetric density,

$$F(q) = \frac{4\pi}{q}\int dr \ r\,\rho(r)\ \sin(qr). \tag{434}$$

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

$$F(q) = Q - \frac{1}{6}\,q^2\,\langle r^2\rangle + \ldots, \tag{435}$$

where

$$Q = \int d^3r \ \rho(r), \tag{436}$$

$$\langle r^2\rangle = \int d^3r \ r^2\,\rho(r). \tag{437}$$

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

  $$\rho(r) = \rho_0 \qquad \text{for } x \le R \tag{438}$$

  (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,

  $$F(q) = \frac{3\,j_1(qR)}{qR}, \tag{439}$$

  where

  $$j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}. \tag{440}$$

  Note that

  $$\frac{3\,j_1(x)}{x} \approx 1 - \frac{1}{10}\,x^2 + \ldots, \tag{441}$$

  and, indeed, the charge radius of a uniform distribution is $\langle r^2\rangle = \frac{3}{5}\,R^2$.

- A (normalized) Yukawa distribution
$$\rho(r) = \frac{\mu^2}{4\pi}\,\frac{e^{-\mu r}}{r}, \tag{442}$$
has as form factor
$$F(q) = \frac{\mu^2}{q^2+\mu^2} = \frac{1}{1+q^2/\mu^2}, \tag{443}$$
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
$$\rho(r) = \frac{\mu^3}{8\pi}\,e^{-\mu r}, \tag{444}$$
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
$$F(q) = \frac{1}{(1+q^2/\mu^2)^2}, \tag{445}$$
which is called a *dipole* form factor.

- Finally a normalized Gaussian distribution
$$\rho(r) = \rho_0\, e^{-\frac{1}{2}\,r^2/R^2} \tag{446}$$
has also a Gaussian form factor
$$F(q) = e^{-\frac{1}{2}\,q^2\,R^2}. \tag{447}$$

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Exercise: 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 $R = 0.8\times10^{-15}$ 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 ($\lambda\!\!\!^{-}_e = \hbar/m_e c \approx 4\times10^{-13}$ m).

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18 Time-independent scattering solutions

18.1 Asymptotic behavior and relation to cross section

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

$$\left(\boldsymbol{\nabla}^2 + k^2\right)\phi(\boldsymbol{r}) = \frac{2m}{\hbar^2}\,V(\boldsymbol{r})\,\phi(\boldsymbol{r}), \tag{448}$$

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,

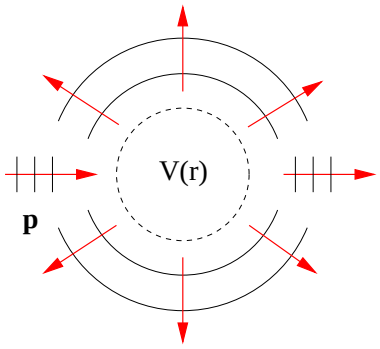
$$\left(\boldsymbol{\nabla}^2 + k^2\right)\phi_{\rm hom}(\boldsymbol{r}) = 0. \tag{449}$$

The solutions of the homogeneous equation are well-known, namely the plane waves,

$$\phi_k(\boldsymbol{r}) = \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}),$$

characterized by a wave vector $\boldsymbol{k}$. This plane wave can be expanded in terms of spherical harmonics multiplying spherical Bessel functions, which will be used to treat scattering problems using a *Partial Wave Expansion*.

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,

$$\phi(\boldsymbol{r}) \quad \stackrel{r\to\infty}{\longrightarrow} \quad \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) + \frac{e^{i\,kr}}{r}\,f(k;\theta,\phi). \tag{450}$$

We have seen in the previous chapter that for $r \to \infty$, this is a solution of the homogeneous equation.

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Exercise: For the second part in the above ansatz one has to be aware that one makes the ansatz for $r \to \infty$. One can simply check that the above represents a solution in this limit 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

$$\boldsymbol{j}_{in} = \frac{\hbar \boldsymbol{k}}{m}, \tag{451}$$

while the second part up to $\mathscr{O}(1/r)$ corresponds with a radially outward directed flux of magnitude

$$j_r = -\frac{i\hbar}{2m}\left[\phi^* \frac{d}{dr}\phi - \left(\frac{d}{dr}\phi^*\right)\phi\right] = \frac{\hbar k}{m}\,\frac{|f(k;\theta,\phi)|^2}{r^2}. \tag{452}$$

From it, one derives the cross section using that

$$|j_{in}|\, d\sigma(\theta,\phi) = n(\theta,\phi)\, d\Omega = j_r\, r^2\, d\Omega, \tag{453}$$

i.e.

$$\frac{d\sigma}{d\Omega} = |f(k;\theta,\phi)|^2. \tag{454}$$

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,

$$\mathscr{I}m\, f_{el}(\theta = 0) = \frac{k}{4\pi}\,\sigma_T, \tag{455}$$

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. 450. 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:

$$\begin{aligned}
&\mathscr{R}e\int_{-1}^{1} dX\;(1+X)\,\frac{e^{i\,kr(1-X)}}{r}\,f \\
&\qquad = \mathscr{R}e\int_{-1}^{1} d\left(e^{i\,kr(1-X)}\right)\;\frac{(1+X)f}{-i\,kr^2} \\
&\qquad = \mathscr{R}e\left(\frac{2\,f(k;\theta=0)}{-i\,kr^2}\right) - 2\mathscr{R}e\int_{-1}^{1} dX\;\frac{e^{i\,kr(1-X)}}{-i\,kr^2}\,\frac{d}{dX}\left[(1+X)f\right] \\
&\qquad = -\frac{2\,\mathscr{I}m\, f(k;\theta=0)}{kr^2} + \mathscr{O}\left(\frac{1}{r^3}\right).
\end{aligned}$$

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

$$\int d\Omega\; j_r\Big|_{r=R} = \frac{1}{R^2}\left[\int d\Omega\;|f|^2 - \frac{4\pi}{k}\,\mathscr{I}m\, f(k;\theta=0)\right],$$

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.

18.2 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

$$\left(\boldsymbol{\nabla}^2 + k^2\right) G(\boldsymbol{r}, \boldsymbol{r}') = -\delta^3(\boldsymbol{r} - \boldsymbol{r}'). \tag{456}$$

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

$$G^{(\pm)}(\boldsymbol{r} - \boldsymbol{r}') = -\frac{\exp\left(\pm i\, k|\boldsymbol{r} - \boldsymbol{r}'|\right)}{4\pi\, |\boldsymbol{r} - \boldsymbol{r}'|}. \tag{457}$$

Note that the difference between these two is a solution of the homogeneous equation.

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Exercise: In this exercise we look at the ingredients needed to find the Green function for the 3-dimensional Schrödinger equation.

(a) Show that

$$\boldsymbol{\nabla}^2 \left(\frac{1}{r}\right) = 0 \quad \text{if } r \neq 0 \qquad \text{and} \qquad \int d^3r \; \nabla^2 \left(\frac{1}{r}\right) = -4\pi,$$

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 the inhomogeneous equation which on the righthandside has $\boldsymbol{\delta}^3(\boldsymbol{r} - \boldsymbol{r}')$ 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 $G(\boldsymbol{r}) = e^{\pm ikr}/4\pi\, r$ are solutions of the equation under (b).

==========

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 the write the scattering solution

$$\phi(\boldsymbol{r}) = \exp(i\, \boldsymbol{k} \cdot \boldsymbol{r}) - \frac{m}{2\pi\, \hbar^2} \int d^3r' \; \frac{\exp\left(+i\, k|\boldsymbol{r} - \boldsymbol{r}'|\right)}{|\boldsymbol{r} - \boldsymbol{r}'|}\, V(\boldsymbol{r}')\, \phi(\boldsymbol{r}'). \tag{458}$$

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 $r \to \infty$ 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

$$\phi_{\rm sc}^{(+)}(\boldsymbol{r}) \quad \stackrel{r\to\infty}{\longrightarrow} \quad \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) - \frac{e^{i\,kr}}{r}\,\frac{m}{2\pi\,\hbar^2}\int d^3r'\;\exp\left(-i\,\boldsymbol{k}'\cdot\boldsymbol{r}'\right)\;V(\boldsymbol{r}')\,\phi_{\rm sc}^{(+)}(\boldsymbol{r}'). \tag{459}$$

and thus the exact expression is

$$f(k;\theta,\phi) = -\frac{m}{2\pi\,\hbar^2}\int d^3r'\;\exp\left(-i\,\boldsymbol{k}'\cdot\boldsymbol{r}'\right)\;V(\boldsymbol{r}')\,\phi_{\rm sc}^{(+)}(\boldsymbol{r}'). \tag{460}$$

18.3 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

$$f(k;\theta,\phi) = -\frac{m}{2\pi\,\hbar^2}\int d^3r'\;\exp\left(i\,\boldsymbol{q}\cdot\boldsymbol{r}'\right)\;V(\boldsymbol{r}'), \tag{461}$$

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,

$$T = V + V\,\tilde{G}\,T, \tag{462}$$

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*

$$f(k;\theta,\phi) = -\frac{m}{2\pi\,\hbar^2}\,\langle\boldsymbol{p}'|T|\boldsymbol{p}\rangle. \tag{463}$$

The lowest order (Born approximation) result is the first term in the expansion obtained from Eq. 462,

$$T = V + V\,\tilde{G}\,V + V\,\tilde{G}\,V\,\tilde{G}\,V + \ldots.$$

To judge the validity of the Born approximation one requires that the scattering term in the wave function is small, i.e.

$$\frac{m}{2\pi\,\hbar^2}\left|\int d^3r'\;\frac{\exp\left(i\,k|\boldsymbol{r}-\boldsymbol{r}'|\right)}{|\boldsymbol{r}-\boldsymbol{r}'|}\,V(\boldsymbol{r}')\,\phi_{\rm sc}^{(+)}(\boldsymbol{r}')\right| \ll 1. \tag{464}$$

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

$$\left| \int d^3r' \; \frac{\exp\left(i\,kr' + i\,\boldsymbol{k}\cdot\boldsymbol{r}'\right)}{r'}\, V(\boldsymbol{r}') \right| \ll \frac{2\pi\,\hbar^2}{m}$$
$$\left| 2\pi \int_{-1}^{1} dX \int dr' \; r'\, e^{i\,kr'(1+X)}\, V(r') \right| \ll \frac{2\pi\,\hbar^2}{m},$$
$$\left| \int dr' \; \left(e^{2i\,kr'} - 1 \right) V(r') \right| \ll \frac{\hbar^2 k}{m} = \hbar v.$$

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.

$$V_0 \ll \frac{\hbar^2}{m\,a^2}, \tag{465}$$

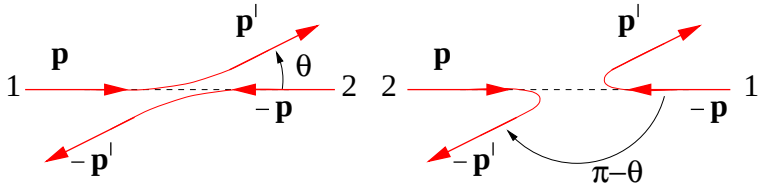
  a condition where an approximately equal sign usually is already ok.

- 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.

$$ka \gg \frac{m\,V_0\,a^2}{\hbar^2} \qquad \text{or} \qquad E \gg \frac{m\,V_0^2\,a^2}{\hbar^2}. \tag{466}$$

18.4 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 $\pi - \theta$,

$$\phi_{12}(\boldsymbol{r}) = e^{i\,kz} + f(k;\theta,\phi)\,\frac{e^{i\,kr}}{r}, \tag{467}$$

$$\phi_{21}(\boldsymbol{r}) = e^{-i\,kz} + f(k;\pi-\theta,\phi+\pi)\,\frac{e^{i\,kr}}{r}, \tag{468}$$

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,

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= |f(k;\theta) \pm f(k;\pi-\theta)|^2 \\ &= |f(k;\theta)|^2 + |f(k;\pi-\theta)|^2 \pm 2\,\mathscr{R}e\left[f^*(k;\theta)\, f(k;\pi-\theta)\right], \end{aligned} \tag{469}$$

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 $0 \leq \theta \leq \pi/2$ 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

$$\frac{d\sigma_s}{d\Omega} = |f_s(\theta) + f_s(\pi-\theta)|^2, \tag{470}$$

$$\frac{d\sigma_t}{d\Omega} = |f_t(\theta) - f_t(\pi-\theta)|^2, \tag{471}$$

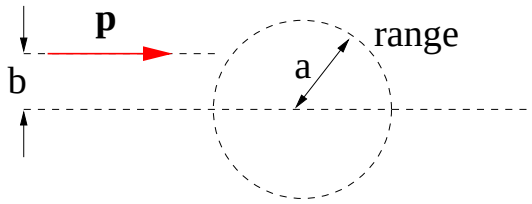
If one scatters unpolarized electrons, the initial state has a probability 1/4 to be in the singlet state, 3/4 to be in the triplet state, thus for a spin-independent potential

$$\frac{d\sigma}{d\Omega} = \frac{1}{4}\,\frac{d\sigma_s}{d\Omega} + \frac{3}{4}\,\frac{d\sigma_t}{d\Omega} = |f(k;\theta)|^2 + |f(k;\pi-\theta)|^2 - \mathscr{R}e\left[f(k;\theta)\, f^*(k;\pi-\theta)\right]. \tag{472}$$

19 Partial wave expansion

19.1 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 $b \leq a$. From this we obtain $\hbar\ell \leq pa = \hbar ka$ or $\ell \leq ka$. 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

$$e^{ikz} = \sum_\ell (2\ell+1)\, i^\ell\, j_\ell(kr)\, P_\ell(\cos\theta). \tag{473}$$

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,

$$f(k;\theta) = \sum_\ell (2\ell+1)\, f_\ell(k)\, P_\ell(\cos\theta). \tag{474}$$

Thus one obtains

$$\phi_{sc}(\boldsymbol{r}) \quad \stackrel{r\to\infty}{\longrightarrow} \quad \sum_\ell (2\ell+1)\, P_\ell(\cos\theta)\, i^\ell \underbrace{\left[j_\ell(kr) + (-i)^\ell \frac{e^{i\,kr}}{r}\, f_\ell(k) \right]}_{\phi_{sc}^{(\ell)}(r)}. \tag{475}$$

Rewriting the scattering wave in the following way,

$$\begin{aligned} \phi_{sc}^{(\ell)}(\boldsymbol{r}) \quad &\stackrel{r\to\infty}{\longrightarrow} \quad \frac{\sin(kr - \ell\pi/2)}{kr} + (-i)^\ell \frac{e^{i\,kr}}{r}\, f_\ell(k) \\ &= \quad \frac{1}{2i\,k}\left[-\frac{e^{-i(kr-\ell\pi/2)}}{r} + \frac{e^{i(kr-\ell\pi/2)}}{r}\,(1 + 2i\,k f_\ell(k)) \right], \end{aligned} \tag{476}$$

Conservation of flux tells us that the incoming and outgoing fluxes should be equal in magnitude, i.e.

$$1 + 2i\,k f_\ell(k) \equiv e^{2i\,\delta_\ell(k)}, \tag{477}$$

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

$$f_\ell(k) = \frac{e^{2i\,\delta_\ell(k)} - 1}{2i\,k} = \frac{e^{i\,\delta_\ell(k)}\, \sin\delta_\ell(k)}{k}, \tag{478}$$

and

$$\phi_{sc}^{(\ell)}(\boldsymbol{r}) \quad \stackrel{r\to\infty}{\longrightarrow} \quad e^{i\,\delta_\ell(k)}\, \frac{\sin(kr - \ell\pi/2 + \delta_\ell(k))}{kr}. \tag{479}$$

==========

Exercise: In fact a phase shift is a characteristic feature of a one-dimensional problem if one only has reflection. You may remember the following problem, in which one investigates 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 $x \geq 0$ as

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

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

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

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

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.

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

==========

19.2 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

$$1 + 2i\,k f_\ell(k) \equiv \eta_\ell\, e^{2i\,\delta_\ell(k)}, \tag{480}$$

where η_ℓ is called the *elasticity*. One then has for the elastic cross section

$$\frac{d\sigma_{el}}{d\Omega} = |f(k;\theta)|^2 = 4\pi \sum_{\ell,\ell'} \sqrt{(2\ell+1)(2\ell'+1)}\, f_\ell(k)\, f_{\ell'}(k)\, Y_\ell^{0*}(\theta)\, Y_{\ell'}^0(\theta). \tag{481}$$

Integrating over angles the orthonormality of the Y_ℓ^m's can be used to get

$$\sigma_{el} = \frac{4\pi}{k^2} \sum_\ell (2\ell+1)\, \sin^2 \delta_\ell(k) \tag{482}$$

Via the optical theorem, which relates the forward scattering amplitude to the total cross section one finds

$$\sigma_T = \frac{2\pi}{k^2} \sum_\ell (2\ell+1)\,(1 - \eta_\ell\, \cos 2\delta_\ell), \tag{483}$$

which indeed is identical for purely elastic scattering ($\eta_\ell = 1$). The difference is the inelastic cross section,

$$\sigma_{inel} = \frac{\pi}{k^2} \sum_\ell (2\ell+1)\,(1 - \eta_\ell^2). \tag{484}$$

19.3 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 $r \leq a$ and zero elsewhere. We immediately know that for $r \geq a$ 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

$$\phi_{\ell m}(\boldsymbol{r}) = \frac{u_\ell(r)}{r}\, Y_\ell^m(\theta,\phi), \tag{485}$$

we have

$$\left[-\frac{\hbar^2}{2m}\,\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} + V(r)\right] u_\ell(r) = E\, u_\ell(r). \tag{486}$$

Knowing that $u_\ell(0) = 0$ we obtain for s-waves ($\ell = 0$)

$$\begin{aligned} r \leq a \qquad & u(r) = A\, \sin Kr \qquad \text{with } K = \sqrt{\frac{2m}{\hbar^2}\,(E - V_0)}, \\ r \geq a \qquad & u(r) = B\, \sin(kr + \delta_0) \quad \text{with } k = \sqrt{\frac{2m}{\hbar^2}\,E}, \end{aligned}$$

Matching the logarithmic derivative $(du/dr)/u(r)$ at $r = a$ gives

$$\tan(ka + \delta_0) = \frac{k}{K}\, \tan Ka \tag{487}$$

or

$$\tan\delta_0(k) \qquad = \qquad \frac{\frac{k}{K}\,\tan Ka - \tan ka}{1 + \frac{k}{K}\,\tan Ka\,\tan ka} \tag{488}$$

$$\stackrel{ka \ll 1}{\longrightarrow} \qquad \frac{ka\left[\frac{\tan Ka}{Ka} - 1\right]}{1 + (ka)^2\,\frac{\tan Ka}{Ka}}, \tag{489}$$

$$\stackrel{Ka \ll 1}{\longrightarrow} \qquad ka\left[\frac{\tan Ka}{Ka} - 1\right] \approx \frac{K^2\, a^3}{3}\, k \tag{490}$$

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,

$$\delta_0(k) = a_0\, k + \frac{1}{2}\, r_e\, k^2 + \ldots, \tag{491}$$

have specific names, namely *scattering length* and *effective range*, respectively.

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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.

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Exercise: 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 and the s-wave contribution to the cross section (consider what happens in the limit that V_0 becomes very strong or very weak).

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20 Relativity and Quantum Mechanics

20.1 Lorentz transformations

In section **??** we have seen the Gallilei transformations. The 10 generators of the Gallilei transformations have specific commutation relations which are similar as operators in space-time and as operators in Hilbert space. For the operators in Hilbert space the expectation value is time-independent.

For a relativistic theory the relevant transformations are the Poincaré transformations, consisting of four (space and time) translations, three rotations and three boosts, the latter six transformations are also referred to as Lorentz transformations. The difference with the Gallilei transformations is in the boosts, which in the relativistic situation mix space and time, explicitly for a boost in the z-direction, we have

Special Gallilean transformation	Lorentz boost
$ct' = ct$	$ct' = \gamma\, ct - \beta\gamma\, z,$
$x' = x$	$x' = x,$
$y' = y$	$y' = y,$
$z' = z - \beta\, ct$	$z' = \gamma\, z - \beta\gamma\, ct,$

where we work with ct (multiplied with the velocity of light c) such that all coordinates have the same dimensions. The quantity $\beta = u_z/c$ corresponds to the boost velocity (divided by c). Hence, there are three boosts. The quantity $\gamma = 1/\sqrt{1-\boldsymbol{\beta}^2}$. It is easy to see that $c^2\, t^2 - \boldsymbol{x}^2$ is invariant, telling us that the velocity of light

$$c \;=\; 299\;792\;458 \text{ m s}^{-1}, \tag{492}$$

is the same in any reference frame), if $x = ct$ then also $x' = ct'$. The quantity

$$x^2 = x \cdot x = c^2t^2 - \boldsymbol{x}^2 = c^2t^2 - x^2 - y^2 - z^2, \tag{493}$$

is called the *invariant length* of the four-vector $(x^\mu) = (x^0, \boldsymbol{x}) = (ct, x, y, z)$, which lives in Minkowski space (see Appendix B). Its invariance is actually the definition of Lorentz transformations. Lorentz transformations thus include the three boosts and three rotations, where the latter are a subgroup that does not affect time and leaves $\boldsymbol{x}^2 = x^2 + y^2 + z^2$ invariant. While rotations mix two coordinates in a plane, the boosts mix time with any of the spatial coordinates. Because of the minus sign in the definition of the invariant length, one sees that while the rotations can be parametrized using the cosine and sine of an angle α, the boost can be naturally written as cosine and sine hyperbolic of an real number η, known as *rapidity*. Considering rotations around z-axis and boosts in z-direction,

Rotations	Boosts
$ct' = ct$	$ct' = \cosh(\eta)\, ct - \sinh(\eta)\, z,$
$x' = \cos(\alpha)\, x - \sin(\alpha)\, y$	$x' = x,$
$y' = \sin(\alpha)\, x + \cos(\alpha)\, y$	$y' = y,$
$z' = z$	$z' = -\sinh(\eta)\, ct + \cosh(\eta)\, z,$

thus $\gamma = \cosh(\eta)$ and $\beta\gamma = \sinh(\eta)$. From the explicit matrices in Minkowski space, one can also find the generators and their commutation relations. We have for rotations around the z-axis $\Lambda_R(\alpha, \hat{z}) =$

$\exp(i\,\varphi\,J^3)$, infinitesimally given by $\Lambda_R(\alpha,\hat{z}) \approx I - i\,\alpha\,J^3$. Thus

$$\Lambda_R(\alpha,\hat{z}) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha & 0 \\ 0 & \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad \longrightarrow \quad J^3 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{494}$$

For boosts along the z-direction we have $\Lambda_B(\eta,\hat{z}) = \exp(+i\,\eta\,cK^3)$, infinitesimally given by $\Lambda_B(\eta,\hat{z}) \approx I + i\,\eta\,cK^3$. Explicitly we have

$$\Lambda_B(\eta,\hat{z}) = \begin{pmatrix} \cosh\eta & 0 & 0 & -\sinh\eta \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -\sinh\eta & 0 & 0 & \cosh\eta \end{pmatrix} \quad \longrightarrow \quad cK^3 = \begin{pmatrix} 0 & 0 & 0 & i \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix}. \tag{495}$$

In this way one finds all generators for the Lorentz transformations and one can determine their commutation relations,

$$\begin{aligned} &[J^i, J^j] = i\,\epsilon^{ijk}\,J^k, \\ &[J^i, K^j] = i\,\epsilon^{ijk}\,K^k, \\ &[K^i, K^j] = -i\,\epsilon^{ijk}\,J^k/c^2. \end{aligned}$$

==========

Exercise: Include translations and denoting their generators as $P = (P^\mu) = (H/c, \boldsymbol{P})$, one can look at the generators of the Poincaré transformations. Convince yourself that they satisfy the commutation relations

$$\begin{aligned} &[P^i, P^j] = [P^i, H] = [J^i, H] = 0, \\ &[J^i, J^j] = i\,\epsilon^{ijk}J^k, \quad [J^i, P^j] = i\,\epsilon^{ijk}P^k, \quad [J^i, K^j] = i\,\epsilon^{ijk}K^k, \\ &[K^i, H] = i\,P^i, \quad [K^i, K^j] = -i\,\epsilon^{ijk}J^k/c^2, \quad [K^i, P^j] = i\,\delta^{ij}H/c^2. \end{aligned} \tag{496}$$

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20.2 Symmetry generators in Relativistic Quantum Mechanics

In non-relativistic quantum mechanics, the symmetry operators in Hilbert space satisfied the appropriate commutation relations after introducing momentum operators $(p^\mu) = (i\hbar\,\partial^\mu) = (H/c, \boldsymbol{p})$ and imposing canonical commutation operators. A quantum theory starting with positions $\boldsymbol{r}$ as relevant degrees of freedom, with (nonzero) commutation relations $[r^i, p^j] = i\hbar\,\delta^{ij}$ and $[s^i, s^j] = i\hbar\,\epsilon^{ijk}s^k$, and with $H = \boldsymbol{p}^2/2m$ is consistent with the requirements of Galilean invariance.

This can be extended to a relativistic theory for a free particle, in which case the generators of the Poincaré group are given by

$$\begin{aligned} H &= \sqrt{\boldsymbol{p}^2\,c^2 + m^2\,c^4}, \\ \boldsymbol{P} &= \boldsymbol{p}, \\ \boldsymbol{J} &= \boldsymbol{r} \times \boldsymbol{p} + \boldsymbol{s}, \\ \boldsymbol{K} &= \frac{1}{2c^2}\,(\boldsymbol{r}H + H\boldsymbol{r}) - t\boldsymbol{p} + \frac{\boldsymbol{p} \times \boldsymbol{s}}{H + mc^2}. \end{aligned} \tag{497}$$

As soon as one wants to extend this to a theory for more degrees of freedom with interactions, one runs into problems, such as the fact that interactions are needed not only in the Hamiltonian, but also in the boost operator. These do not matter in the non-relativistic limit ($c \to \infty$), that's why many-particle non-relativistic quantum mechanics is 'easy'.

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Exercise: Check the commutation relations for $[J^1, K^2]$ and for $[K^1, K^2]$ starting from the canonical commutators.

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Note that in a function space of functions $f(x) = f(t, \boldsymbol{x})$ the generators of boosts and translations are

$$M^{\mu\nu} = i\hbar(x^\mu \partial^\nu - x^\nu \partial^\mu),$$

for boosts and rotations. One has $J^3 = M^{12}$ and $cK^3 = M^{30}$. It illustrates that, in Minkowski space, the tensor nature of the rotations and boosts is that of an antisymmetrix second rank tensor. In Euclidean space the $J^i = \frac{1}{2}\epsilon^{ijk}M^{jk}$ and $cK^i = M^{i0}$ are three-vectors.

==========

20.3 Relativistic equations

It is not that hard to get relativistic equations. We will discuss the examples of the Klein-Gordon equation and the Dirac equation, starting with an *covariant* equation (valid in any reference frame). Consider, for example, the relation

$$E = mc^2 + \frac{\boldsymbol{p}^2}{2m}.$$

It makes sense in classical mechanics. It involves scalar quantities such as the energy E and a vector quantity $\boldsymbol{p}$. In the equation both sides are scalars. But it doesn't make sense in a relativistic theory. In a relativistic theory one has scalars, such as mass m, four-vectors such as $x = (x^\mu) = (ct, \boldsymbol{x})$ or $p = (p^\mu) = (E/c, \boldsymbol{p})$. The above equation then relates a zero component of a four-vector to something else.

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If you really want to see that the equation is not invariant, just apply a Lorentz boost on the four-momentum $p = (mc, \boldsymbol{0})$ which gives $p = (mc\gamma, mc\beta\gamma)$ and see that the equation is not covariant.

==========

A covariant wave equation for a wave function can be obtained by making the covariant equation $p^\mu p_\mu = m^2$ into an operator acting on the wave function under the replacement

$$p^\mu \longrightarrow i\hbar\,\partial^\mu,$$

which implies $p^0 = E/c \to i\hbar\,\partial^0 = i\hbar\,\partial/\partial t$ and $p^i \to i\hbar\,\partial^i = -i\hbar\,\partial_i$ or $\boldsymbol{p} \to -i\hbar\,\boldsymbol{\nabla}$. The result acting on a wave function is

$$\left(\hbar^2\partial^\mu\partial_\mu + m^2c^2\right)\psi(x) = \left(\hbar^2\Box + m^2c^2\right)\psi(x) = \left(\frac{\hbar^2}{c^2}\frac{\partial^2}{\partial t^2} - \hbar^2\boldsymbol{\nabla}^2 + m^2c^2\right)\psi(x) = 0,$$

which is known as the Klein-Gordon equation.

It will turn out that in a consistent relativistic theory, the functions $\psi(x)$ in these relativistic equations need a completely different interpretation. They in turn will become operators containing creation and annihilation operators. The x-dependence, however, found by solving the equations, will remain useful, describing the space-time dependence of the modes that can be created. We will look at this space-time dependence and indicate some of the problems that need to be addressed in a full relativistic treatment in the next sections (Chapter 15 of Bransden & Joachain).

21 The Klein-Gordon equation

21.1 Solutions of the Klein-Gordon equation

We have seen how the Klein-Gordon (KG) equation,

$$\left(\hbar^2 c^2 \partial^\mu \partial_\mu + m^2 c^4\right) \psi(x) = \left(\hbar^2 c^2 \Box + m^2 c^4\right) \psi(x) = \left(\hbar^2 \frac{\partial^2}{\partial t^2} - \hbar^2 c^2 \boldsymbol{\nabla}^2 + m^2 c^4\right) \psi(x) = 0, \tag{498}$$

has been constructed as a covariant equation. Indeed, its solutions are easily found to be

$$\psi_k(x) = \exp(-ik \cdot x), \tag{499}$$

or making explicit time and space dependence,

$$\psi_k(\boldsymbol{x}, t) = \exp(-i\omega t + i\boldsymbol{k} \cdot \boldsymbol{x}), \tag{500}$$

where $p = \hbar k$ is the momentum (eigenvalue of $p^\mu = i\,\partial^\mu$), a four-vector that is constraint to be $p^2 = m^2 c^2$. This implies

$$E = \pm\sqrt{\boldsymbol{p}^2 c^2 + m^2 c^4},$$

This infinite number of negative energy states clearly constitutes a problem.

But this is not the only problem with the KG equation. To interpret the function, we want to identify things like density and current, to be precise the components of the four-current $(j^\mu) = (j^0, \boldsymbol{j}) = (c\rho, \boldsymbol{j})$, that satisfy the (covariant) continuity equation,

$$\partial_\mu j^\mu = 0 \quad \text{or} \quad \frac{\partial}{\partial t}\rho = -\boldsymbol{\nabla} \cdot \boldsymbol{j}. \tag{501}$$

==========

Exercise Show that

$$j^\mu = \frac{i\hbar}{2m} \left(\psi^* \,\partial^\mu \psi - (\partial^\mu \psi^*)\psi\right), \tag{502}$$

satisfies the continuity equation if ψ and ψ^* satisfy the Klein-Gordon equation.

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In particular, one has

$$\rho = \frac{i\hbar}{2mc^2} \left(\psi^* \frac{\partial}{\partial t}\psi - \psi \frac{\partial}{\partial t}\psi^*\right). \tag{503}$$

Since ψ is a second order differential equation one can find solutions for any given value for ψ and $\dot{\psi}$ at a given time, thus one not only has negative energies, but also negative densities. These problems are solved by considering the *negative energy modes* as positive energy *anti-particle* modes. The positive energy solutions of the Klein-Gordon equation can be used to describe the wave functions of spin-less (spin zero) particles.

21.2 Charged particle in an electromagnetic field

By *minimal substitution*,

$$i\partial_\mu \longrightarrow i\partial_\mu - q\,A_\mu, \tag{504}$$

where $(A^\mu) = (\phi/c, \boldsymbol{A})$ is the field known from covariant electrodynamics one obtains the KG equation for a particle with charge q in an electromagnetic field,

$$\frac{1}{c^2}\left(i\hbar\frac{\partial}{\partial t} - q\phi\right)^2 \psi = \left((-i\hbar\boldsymbol{\nabla} - q\boldsymbol{A})^2 + m^2c^2\right)\,\psi. \tag{505}$$

It simply follows that introducing

$$\psi(\boldsymbol{x}, t) = e^{-i\,mc^2\,t/\hbar}\,\psi_{\rm NR}(\boldsymbol{x}, t), \tag{506}$$

one gets in the limit that $|q\phi| \ll mc^2$ the nonrelativistic Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}\psi_{\rm NR} = \left(\frac{(-i\hbar\boldsymbol{\nabla} - q\boldsymbol{A})^2}{2m} + q\,\phi\right)\psi_{\rm NR}. \tag{507}$$

==========

Exercise: Show that in the case where the remaining time dependence of $\psi_{\rm NR}$ in Eq. 506 is *slow* enough one gets $\rho = |\psi_{\rm NR}|^2$.

==========

One can actually exactly solve Eq. 505 for stationary solutions with energy E in a central electric field, which are of the form

$$\psi(\boldsymbol{r}, t) = \frac{u(r)}{r}\,Y_\ell^m(\theta, \varphi)\,e^{-iEt/\hbar},$$

satisfying

$$\left(E + \frac{Z\alpha\hbar c}{r}\right)^2 u(r) = \left(\hbar^2c^2\left(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2}\right) + m^2c^4\right)u(r), \tag{508}$$

or

$$\left(\hbar^2c^2\left(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1) - Z^2\alpha^2}{r^2}\right) - \frac{2E\,Z\alpha\,\hbar c}{r} - (E^2 - m^2c^4)\right)u(r) = 0. \tag{509}$$

==========

Exercise: By mapping this into a 'generalized Laguerre polynomial' form show that one finds solutions with energies

$$E_{n\ell} = \frac{mc^2}{\sqrt{1 - \frac{Z^2\alpha^2}{(n-\delta_\ell)^2}}}, \tag{510}$$

where $\delta_\ell = \ell + 1/2 - \sqrt{(\ell+1/2)^2 - Z^2\alpha^2}$.

==========

22 The Dirac equation

To solve the problem with positive and negative energies and get a positive definite density, an attempt to construct a first order differential equation for the time evolution would be to write,

$$i\,\frac{\hbar}{c}\frac{\partial}{\partial t}\psi(\boldsymbol{r},t) = (-i\hbar\,\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + mc\,\beta)\,\psi(\boldsymbol{r},t), \tag{511}$$

where ψ is a wave function and the nature of $\boldsymbol{\alpha}$ and β (numbers, matrices, ...) is left open for the moment.

==========

Exercise: Show that relativistic invariance, i.e. making sure that each component of ψ satisfies the Klein-Gordon equation (in terms of differential operators $\partial_\mu\partial^\mu + m^2 = 0$) requires the anticommutation relation[7]

$$\{\alpha^i,\alpha^j\} = 2\,\delta^{ij}\,I, \qquad \{\alpha^i,\beta\} = 0, \quad \text{and} \quad \beta^2 = I.$$

==========

From this one concludes that $\boldsymbol{\alpha}$ and β must be matrix-valued and ψ must be a multi-component wave function. Next one might try to see if the positive definite quantity $\psi^\dagger\psi$ (generalization of $\psi^*\psi$ to more components) is suitable to represent a density.

==========

Exercise: Show that one has current conservation for the current

$$j^0 = \psi^\dagger\psi \quad \text{and} \quad \boldsymbol{j} = \psi^\dagger\boldsymbol{\alpha}\psi.$$

==========

Thus, the answer is 'yes', there is a candidate (positive definite) density.

Next problem is covariance. We see that $H = \boldsymbol{\alpha}\cdot\boldsymbol{p}c + mc^2\beta$. To assure covariance we need that β is a zeroth component of a four-vector (of Dirac matrices), $\beta = \gamma^0$. Multiplying Eq. 511 with β and using the requirement (see Exercise above) that $\beta^2 = I$, we rewrite that equation into

$$(i\hbar\gamma^\mu\partial_\mu - mc)\,\psi(x) = 0, \tag{512}$$

the *Dirac equation* where $\boldsymbol{\gamma} = \beta\boldsymbol{\alpha}$ and the Dirac matrices satisfy

$$\{\gamma^\mu,\gamma^\nu\} = 2\,g^{\mu\nu}. \tag{513}$$

We have found a covariant equation, linear in p. The covariant form of the four-current is

$$j = (j^\mu) = (\psi^\dagger\psi, \psi^\dagger\gamma^0\boldsymbol{\gamma}\psi)$$

which is usually written as

$$j^\mu = \overline{\psi}\gamma^\mu\psi, \tag{514}$$

with $\overline{\psi} \equiv \psi^\dagger\gamma^0$. There is no unique set of γ matrices, since one can make arbitrary unitary transformations in Dirac space. We will use the following set (known as the standard representation), which is particularly useful to take the non-relativistic limit,

$$\gamma^0 = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix} = \rho^3\otimes\mathbf{1}, \qquad \gamma^k = \begin{pmatrix} 0 & \sigma^k \\ -\sigma^k & 0 \end{pmatrix} = i\rho^2\otimes\sigma^k. \tag{515}$$

We have used here a (direct) product notation where the 4×4 Dirac matrices are written as direct products $\rho\otimes\sigma$ (with $\otimes$ usually suppressed) of 2×2 Pauli matrices.

[7] We denote the commutator as $[A,B] = AB - BA$ and the anticommutator as $\{A,B\} = AB + BA$.

==========

Using properties of the (three) Pauli matrices (with Euclidean indices), such as

$$\sigma_i\,\sigma_j = \delta_{ij} + i\,\epsilon_{ijk}\,\sigma_k,$$
$$[\sigma_i, \sigma_j] = 2i\,\epsilon_{ijk}\,\sigma_k,$$

one can easily verify the (anti)-commutation relations of the γ-matrices.

==========

Lorentz invariance

We have introduced a four-vector of matrices with components γ^μ. This implies that Lorentz transformations should change this vector in the required way. The resulting operations in Dirac space, $\gamma^\mu \to L\gamma^\mu L^{-1}$ must be such that they have the effect of a boost, thus $L\gamma^\mu L^{-1} = \Lambda^\mu_\nu\,\gamma^\nu$. We will just give the answer for the generators in Dirac space, they are $J^3 = \frac{i}{4}\hbar[\gamma^1, \gamma^2]$, etc. and $cK^3 = \frac{i}{4}\hbar[\gamma^3, \gamma^0]$, etc., or explicitly

$$\boldsymbol{J} = \frac{\hbar}{2}\begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix} = \frac{\hbar}{2}\,\boldsymbol{\Sigma} \quad \text{and} \quad c\boldsymbol{K} = \frac{\hbar}{2}\begin{pmatrix} 0 & -i\,\boldsymbol{\sigma} \\ -i\,\boldsymbol{\sigma} & 0 \end{pmatrix} \tag{516}$$

The contribution to rotations from the internal part is known as spin. The full rotation operator in Dirac space thus is

$$\boldsymbol{J} = \boldsymbol{r} \times \boldsymbol{p} + \boldsymbol{s} = -i\hbar\,\boldsymbol{r} \times \boldsymbol{\nabla} + \frac{\hbar}{2}\,\boldsymbol{\Sigma}. \tag{517}$$

The explicit form of the Hamiltonian is

$$H = \boldsymbol{\alpha}\cdot\boldsymbol{p}c + mc^2\,\beta = \begin{pmatrix} mc^2 & \boldsymbol{\sigma}\cdot\boldsymbol{p}c \\ \boldsymbol{\sigma}\cdot\boldsymbol{p}c & -mc^2 \end{pmatrix} \tag{518}$$

We note that H doesn't commute with $\boldsymbol{L}$ or $\boldsymbol{S}$,

$$[H, \boldsymbol{\ell}] = -i\hbar c\,(\boldsymbol{\alpha} \times \boldsymbol{p}), \tag{519}$$
$$[H, \boldsymbol{s}] = -i\hbar c\,(\boldsymbol{\alpha} \times \boldsymbol{p}), \tag{520}$$

but $[H, \boldsymbol{J}] = 0$ as required by Lorentz invariance for a single particle (without having potentials).

Free particle solutions of Dirac equation

==========

Show, by acting on the Dirac equation with $(i\gamma^\nu\partial_\nu + mc^2)$, using the symmetry of $\partial_\mu\partial_\nu = \partial_\nu\partial_\mu$ and the commutation relations of the γ matrices that a solution of the Dirac equation,

$$(i\hbar\gamma^\mu\partial_\mu - mc)\,\psi(x) = 0,$$

also is a solution of the Klein-Gordon equation

$$\left(\hbar^2\partial^\mu\partial_\mu + m^2c^2\right)\psi(x) = 0.$$

==========

Since the Dirac equation also obeys the Klein-Gordon equation, it also has positive and negative energy solutions. Starting with a plane wave for the space-time dependence, we have solutions

$$\psi(x) = u(p,s)\, e^{ip\cdot x/\hbar} \quad \text{and} \quad \psi(x) = v(p,s)\, e^{-ip\cdot x/\hbar} \tag{521}$$

with positive and negative energies, respectively. Inserting the solutions into the Dirac equation, one gets

$$(\gamma^\mu p_\mu + mc)u(p,s) = 0 \quad \text{and} \quad (\gamma^\mu p_\mu - mc)v(p,s) = 0. \tag{522}$$

Indicating with χ_s and $\overline{\chi}_s$, respectively the two possible two-component spin eigenstates (of σ_z) for these solutions, the explicit solutions are

$$u(p,s) = N \begin{pmatrix} \chi_s \\ \frac{\boldsymbol{\sigma}\cdot\boldsymbol{p}}{E_p+mc^2}\, c\,\chi_s \end{pmatrix} \quad \text{with} \quad E = +E_p = +\sqrt{\boldsymbol{p}^2c^2 + m^2c^4}, \tag{523}$$

and

$$v(p,s) = N \begin{pmatrix} \frac{\boldsymbol{\sigma}\cdot\boldsymbol{p}}{E_p+mc^2}\, c\,\overline{\chi}_s \\ \overline{\chi}_s \end{pmatrix} \quad \text{with} \quad E = -E_p = -\sqrt{\boldsymbol{p}^2c^2 + m^2c^4}. \tag{524}$$

(with usually the normalization taken as $N = \sqrt{E_p + mc^2}$). For a particle in its restframe (three-momentum is zero) one has two positive energy solutions with only upper components and two negative energy solutions with only lower components (interpreted already by Dirac as antiparticle solutions). At any finite momentum, however, the relativistic description will mix upper and lower components, although the mixing of components is suppressed as long as $|\boldsymbol{p}|c \ll mc^2$.

==========

Check that $u(p,s)$ is a solution of $(H - E_p)u(p,s) = 0$.

==========

Dirac equation in an electromagnetic field

Looking for stationary solutions with positive energy, $\psi(x) = \psi(\boldsymbol{r},t) = \psi(\boldsymbol{r})\, e^{-iEt/\hbar}$, we can write the Dirac equation or $(H-E)\psi(x) = 0$ in an electromagnetic field using minimal substitution, $E \to E - q\Phi$ and $\boldsymbol{p} = -i\hbar\boldsymbol{\nabla} \to -i\hbar\boldsymbol{\nabla} - q\boldsymbol{A}$, as

$$\begin{pmatrix} -E_{\rm nr} + q\Phi & \hbar c\,\boldsymbol{\sigma}\cdot(-i\boldsymbol{\nabla} - q\boldsymbol{A}) \\ \hbar c\,\boldsymbol{\sigma}\cdot(-i\boldsymbol{\nabla} - q\boldsymbol{A}) & -2mc^2 - E_{\rm nr} + q\Phi \end{pmatrix} \begin{pmatrix} \psi_{\rm u}(\boldsymbol{r}) \\ \psi_{\rm l}(\boldsymbol{r}) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \tag{525}$$

where $E_{\rm nr} = E - mc^2$. We can write down coupled equations for upper and lower components and use one of them to eliminate (for instance) the lower component, which gives us the Pauli equation,

$$E_{\rm nr}\,\psi_{\rm u}(\boldsymbol{r}) = \hbar^2c^2\,\boldsymbol{\sigma}\cdot(-i\boldsymbol{\nabla} - q\boldsymbol{A})\frac{1}{2mc^2 + E_{\rm nr} - q\Phi}\,\boldsymbol{\sigma}\cdot(-i\boldsymbol{\nabla} - q\boldsymbol{A})\,\psi_{\rm u}(\boldsymbol{r}) + q\Phi\,\psi_{\rm u}(\boldsymbol{r}). \tag{526}$$

We did put explicitly the $1/(2mc^2 + E_{\rm nr} - q\Phi)$ in the middle as it is an operator, of which the inverse can be written in a series,

$$\frac{1}{2mc^2 + E_{\rm nr} - q\Phi} = \frac{1}{2mc^2}\left(1 - \frac{E_{\rm nr} - q\Phi}{2mc^2} + \dots\right).$$

We will consider two cases in more detail.

Spin 1/2 particle in an electromagnetic field

Taking the leading term, we get the non-relativistic limit of the Pauli equation,

$$E_{\rm nr}\,\psi_{\rm u}(\boldsymbol{r}) = \frac{\hbar^2}{2m}\,\boldsymbol{\sigma}\cdot(-i\boldsymbol{\nabla}-q\boldsymbol{A})\,\boldsymbol{\sigma}\cdot(-i\boldsymbol{\nabla}-q\boldsymbol{A})\,\psi_{\rm u}(\boldsymbol{r}) + q\Phi\,\psi_{\rm u}(\boldsymbol{r}). \tag{527}$$

Using $\sigma^i\sigma^j = \delta^{ij} + i\epsilon^{ijk}\sigma^k$, and being careful with the interchange of gradients and $\boldsymbol{A}$,

$$i\,\epsilon^{ijk}\partial^i A^j\psi_{\rm u} = i\,\epsilon^{ijk}(\partial^i A^j)\psi_{\rm u} + i\,\epsilon^{ijk}A^j(\partial^i\psi_{\rm u}) = i\,B^k\psi_{\rm u} + i\,\epsilon^{ijk}A^j(\partial^i\psi_{\rm u}),$$

the result is

$$E_{\rm nr}\,\psi_{\rm u}(\boldsymbol{r}) = \frac{\hbar^2(-i\boldsymbol{\nabla}-q\boldsymbol{A})^2}{2m}\,\psi_{\rm u}(\boldsymbol{r}) - \frac{q\hbar}{2m}\boldsymbol{\sigma}\cdot\boldsymbol{B}\,\psi_{\rm u}(\boldsymbol{r}) + q\Phi\,\psi_{\rm u}(\boldsymbol{r}). \tag{528}$$

This shows that the interaction of a spin 1/2 particle for which the spin operator is given by $\boldsymbol{s} = \hbar\boldsymbol{\sigma}/2$ in a magnetic field involves a g-factor, to be precise

$$H_{\rm magnetic} = -g_s\,\frac{q}{2m}\,\boldsymbol{s}\cdot\boldsymbol{B}, \tag{529}$$

with $g_s = 2$.

Higher order corrections in Hydrogen atom

Again we start from the Pauli equation (Eq. 526) considering only the potential $V(r) = q\Phi(r)$, assuming it to be a central potential. We have

$$E_{\rm nr}\,\psi_{\rm u}(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\,(\boldsymbol{\sigma}\cdot\boldsymbol{\nabla})\left(1 - \frac{E_{\rm nr}-V(r)}{2mc^2} + \ldots\right)(\boldsymbol{\sigma}\cdot\boldsymbol{\nabla})\,\psi_{\rm u}(\boldsymbol{r}) + V(r)\,\psi_{\rm u}(\boldsymbol{r}). \tag{530}$$

The first thing to investigate here is the operator combination, where we get contributions because $\boldsymbol{\nabla}V(r) = \hat{\boldsymbol{r}}\,dV/dr$. Furthermore, to assure hermiticity of the Hamiltonian one averages actions of the derivative to right and left, $\boldsymbol{\nabla} \equiv \overleftrightarrow{\boldsymbol{\nabla}} = \overrightarrow{\boldsymbol{\nabla}} - \overleftarrow{\boldsymbol{\nabla}}$,

$$\begin{aligned}
(\boldsymbol{\sigma}\cdot\overleftrightarrow{\boldsymbol{\nabla}})V(r)(\boldsymbol{\sigma}\cdot\overleftrightarrow{\boldsymbol{\nabla}}) &= \frac{1}{2}\left(\overleftarrow{\boldsymbol{\nabla}}^{\,2}V(r) + V(r)\,\overrightarrow{\boldsymbol{\nabla}}^{\,2}\right) - (\boldsymbol{\sigma}\cdot\boldsymbol{r})\frac{1}{2r}\frac{dV}{dr}(\boldsymbol{\sigma}\cdot\overrightarrow{\boldsymbol{\nabla}}) - (\boldsymbol{\sigma}\cdot\overleftarrow{\boldsymbol{\nabla}})\frac{1}{2r}\frac{dV}{dr}(\boldsymbol{\sigma}\cdot\boldsymbol{r}) \\
&= \frac{1}{2}\left(\overleftarrow{\boldsymbol{\nabla}}^{\,2}V(r) + V(r)\,\overrightarrow{\boldsymbol{\nabla}}^{\,2}\right) - i\left\{\boldsymbol{\sigma}\cdot(\boldsymbol{r}\times\boldsymbol{\nabla}), \frac{1}{2r}\frac{dV}{dr}\right\} - \left\{\frac{1}{2r}\frac{dV}{dr}, r\frac{\partial}{\partial r}\right\} \\
&= \frac{1}{2}\left(\overleftarrow{\boldsymbol{\nabla}}^{\,2}V(r) + V(r)\,\overrightarrow{\boldsymbol{\nabla}}^{\,2}\right) + \frac{1}{r}\frac{dV}{dr}\,\frac{\boldsymbol{\ell}\cdot\boldsymbol{\sigma}}{\hbar} - \frac{1}{2}\,\boldsymbol{\nabla}^2V.
\end{aligned}$$

(note derivatives without arrows act to the right or to the left with a opposite sign). It gives precisely all correction terms discussed for Hydrogen,

$$H = -\frac{\boldsymbol{p}_{\rm op}^2}{2m} + V(r) - \frac{1}{4mc^2}\left\{\frac{\boldsymbol{p}_{\rm op}^2}{2m}, \frac{\boldsymbol{p}_{\rm op}^2}{2m}\right\} + \frac{1}{2m^2c^2}\,\frac{1}{r}\frac{dV}{dr}\,\boldsymbol{\ell}\cdot\boldsymbol{s} + \frac{\hbar^2}{8m^2c^2}\,\boldsymbol{\nabla}^2V(r). \tag{531}$$

This Hamiltonian shows the relativistic corrections, such as the $\boldsymbol{p}^4$ term for the kinetic energy, the spin-orbit interactions and the Darwin term. This last term is for the Coulomb interaction given by

$$H_{\rm Darwin} = \frac{\pi\,\hbar^3}{2m^2c}\,Z\alpha\,\delta^3(\boldsymbol{r}). \tag{532}$$

A 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

$$y'' + g_0(x)\, y = 0 \qquad \text{with} \quad g_0(x) = \left[\frac{2p+a+1}{2x} + \frac{1-a^2}{4x^2} - \frac{1}{4}\right], \tag{533}$$

are given by

$$y(x) = e^{-x/2}\, x^{(a+1)/2}\, L_p^a(x). \tag{534}$$

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

$$\int_0^\infty dx\; x^{a+1}\, e^{-x}\; \left[L_p^a(x)\right]^2 = (2p+a+1)\,\frac{(p+a)!}{p!}, \tag{535}$$

and also satisfy the differential equation

$$\left[x\,\frac{d^2}{dx^2} + (a+1-x)\,\frac{d}{dx} + p\right] L_p^a(x) = 0. \tag{536}$$

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

$$L_p(x) \equiv L_p^0(x) = \frac{e^x}{p!}\,\frac{d^p}{dx^p}\left[x^p\, e^{-x}\right] = \frac{1}{p!}\,\left(\frac{d}{dx} - 1\right)^p\, x^p, \tag{537}$$

$$L_p^a(x) = (-)^a\,\frac{d^a}{dx^a}\left[L_{p+a}(x)\right]. \tag{538}$$

Some general expressions are

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

Some recursion relations are

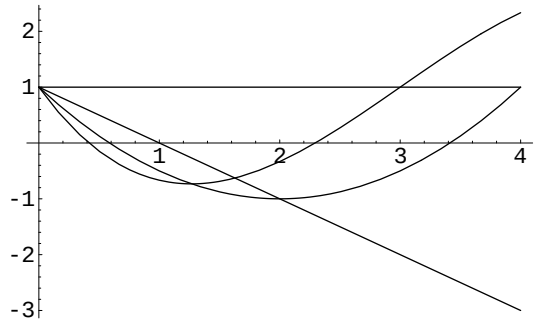
$$(p+1)\, L_{p+1}^a(x) = (2p+a+1-x)\, L_p^a(x) - (p+a)\, L_{p-1}^a(x), \tag{539}$$

$$x\, L_p^{a+1}(x) = (x-p)\, L_p^a(x) + (p+a)\, L_{p-1}^a(x), \tag{540}$$

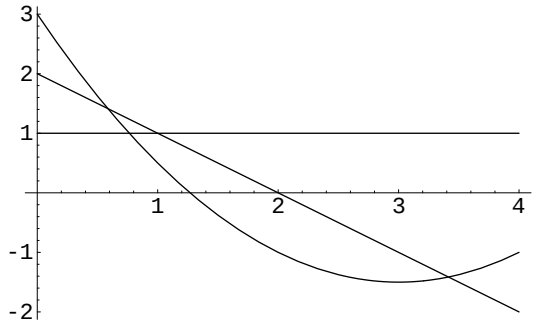
$$L_p^a(x) = L_p^{a-1}(x) + L_{p-1}^a(x). \tag{541}$$

Some explicit polynomials are

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



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



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

B Three-vectors, four-vectors and tensors

We start with vectors in Euclidean 3-space E(3). A vector $\boldsymbol{x}$ can be expanded with respect to a basis $\hat{\boldsymbol{e}}_i$ ($i = 1, 2, 3$ or $i =$ x, y, z),

$$\boldsymbol{x} = \sum_{i=1}^{3} x_i \, \hat{\boldsymbol{e}}_i = x_i \, \hat{\boldsymbol{e}}_i, \tag{542}$$

to get the three components of a vector, x_i. When a repeated index appears, such as on the right hand side of this equation, summation over this index is assumed (Einstein summation convention). Choosing an orthonormal basis, the metric in E(3) is given by $\hat{\boldsymbol{e}}_i \cdot \hat{\boldsymbol{e}}_j = \delta_{ij}$, where the Kronecker delta is given by

$$\delta_{ij} \;=\; \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j, \end{cases} \quad . \tag{543}$$

The inner product of two vectors is given by

$$\boldsymbol{x} \cdot \boldsymbol{y} = x_i \, y_i \, \hat{\boldsymbol{e}}_i \cdot \hat{\boldsymbol{e}}_j = x_i \, y_j \, \delta_{ij} = x_i y_i. \tag{544}$$

The inner product of a vector with itself gives its length squared. A vector can be rotated, $\boldsymbol{x}' = R\boldsymbol{x}$ or $x'_i = R_{ij} x_j$ leading to a new vector with different components. Actually, *rotations* are those *real*, *linear* transformations that do not change the length of a vector. Tensors of rank n are objects with n components that transform according to $T'_{i_1 \ldots i_n} = R_{i_1 j_1} \ldots R_{i_n j_n} \, T_{j_1 \ldots j_n}$. A vector is a tensor of rank 1. The inner product of two vectors is a rank 0 tensor or scalar. The Kronecker delta is a constant rank-2 tensor. It is an invariant tensor that does not change under rotations. The only other invariant constant tensor in E(3) is the Levi-Civita tensor

$$\epsilon_{ijk} \;=\; \begin{cases} 1 & \text{if } ijk \text{ is an even permutation of 123} \\ -1 & \text{if } ijk \text{ is an odd permutation of 123} \\ 0 & \text{otherwise.} \end{cases} \tag{545}$$

that can be used in the cross product of two vectors $\boldsymbol{z} = \boldsymbol{x} \times \boldsymbol{y}$, in which case $z_i = \epsilon_{ijk} \, x_j y_k$. Useful relations are

$$\epsilon_{ijk} \, \epsilon_{\ell mn} \;=\; \begin{vmatrix} \delta_{i\ell} & \delta_{im} & \delta_{in} \\ \delta_{j\ell} & \delta_{jm} & \delta_{jn} \\ \delta_{k\ell} & \delta_{km} & \delta_{kn} \end{vmatrix}, \tag{546}$$

$$\epsilon_{ijk} \, \epsilon_{imn} \;=\; \delta_{jm} \, \delta_{kn} - \delta_{jn} \, \delta_{km}, \tag{547}$$

$$\epsilon_{ijk} \, \epsilon_{ijl} \;=\; 2 \, \delta_{kl}. \tag{548}$$

We note that for Euclidean spaces (with a positive definite metric) vectors and tensors there is only one type of indices. No difference is made between upper or lower. So we could have used all upper indices in the above equations. When 3-dimensional space is considered as part of Minkowski space, however, we will use upper indices for the three-vectors.

In special relativity we start with a four-dimensional real vector space E(1,3) with basis $\hat{n}_\mu$ ($\mu =$ 0,1,2,3). Vectors are denoted $x = x^\mu \hat{n}_\mu$. The length (squared) of a vector is obtained from the scalar product,

$$x^2 \;=\; x \cdot x \;=\; x^\mu x^\nu \hat{n}_\mu \cdot \hat{n}_\nu \;=\; x^\mu x^\nu g_{\mu\nu}. \tag{549}$$

The quantity $g_{\mu\nu} \equiv \hat{n}_\mu \cdot \hat{n}_\nu$ is the metric tensor, given by $g_{00} = -g_{11} = -g_{22} = -g_{33} = 1$ (the other components are zero). For four-vectors in Minkowski space we will use the notation with upper indices and write $x = (ct, \boldsymbol{x}) = (x^0, x^1, x^2, x^3)$, where the coordinate $t = x^0$ is referred to as the time component, x^i are the three space components. Because of the different signs occurring in $g_{\mu\nu}$, it is convenient to

distinguish lower indices from upper indices. The lower indices are constructed in the following way, $x_\mu = g_{\mu\nu}x^\nu$, and are given by $(x_0, x_1, x_2, x_3) = (ct, -\boldsymbol{x})$. One has

$$x^2 \;=\; x^\mu x_\mu \;=\; c^2t^2 - \boldsymbol{x}^2. \tag{550}$$

The scalar product of two different vectors x and y is denoted

$$x \cdot y \;=\; x^\mu y^\nu g_{\mu\nu} \;=\; x^\mu y_\mu \;=\; x_\mu y^\mu \;=\; x^0 y^0 - \boldsymbol{x}\cdot\boldsymbol{y}. \tag{551}$$

Within Minkowski space the *real*, *linear* transformations that do not change the length of a four-vector are called the *Lorentz transformations*. These transformations do change the components of a vector, denoted as $V'^\mu = \Lambda^\mu{}_\nu V^\nu$, The (invariant) lengths often have special names, such as *eigentime* τ for the position vector $c^2\tau^2 \equiv x^2 = c^2t^2 - \boldsymbol{x}^2$. The invariant distance between two points x and y in Minkowski space is determined from the length $ds^\mu = (x-y)^\mu$. The *real*, *linear* transformations that leave the length of a vector invariant are called *(homogeneous) Lorentz transformations*. The transformations that leave invariant the distance $ds^2 = c^2dt^2 - (dx^2 + dy^2 + dz^2)$ between two points are called inhomogeneous Lorentz transformations or *Poincaré transformations*. The Poincaré transformations include Lorentz transformations and translations.

Unlike in Euclidean space, the invariant length or distance (squared) is not positive definite. One can distinguish:

- $ds^2 > 0$ (timelike intervals); in this case an inertial system exists in which the two points are at the same space point and in that frame ds^2 just represents the time difference $ds^2 = c^2dt^2$;
- $ds^2 < 0$ (spacelike intervals); in this case an inertial system exists in which the two points are at the same time and ds^2 just represents minus the spatial distance squred $ds^2 = -d\boldsymbol{x}^2$;
- $ds^2 = 0$ (lightlike or null intervals); the points lie on the lightcone and they can be connected by a light signal.

Many other four vectors and tensors transforming like $T'^{\mu_1\cdots\mu_n} = \Lambda^{\mu_1}{}_{\nu_1}\ldots\Lambda^{\mu_n}{}_{\nu_n}T^{\nu_1\cdots\nu_n}$ can be constructed. In Minkowski space, one must distinguish tensors with upper or lower indices and one can have mixed tensors. Relations relating tensor expressions, independent of a coordinate system, are called covariant. Examples are the scalar products above but also relations like $p^\mu = m\,dx^\mu/d\tau$ for the momentum four vector. Note that in this equation one has on left- and righthandside a four vector because τ is a scalar quantity! The equation with $t = x^0/c$ instead of τ simply would not make sense! The momentum four vector, explicitly written as $(p^0, \boldsymbol{p}) = (E/c, \boldsymbol{p})$, is timelike with invariant length (squared) $p^2 = p\cdot p = p^\mu p_\mu = E^2/c^2 - \boldsymbol{p}^2 = m^2c^2$, where m is called the *mass* of the system.

The derivative ∂_μ is defined $\partial_\mu = \partial/\partial x^\mu$ and we have a four vector ∂ with components

$$(\partial_0, \partial_1, \partial_2, \partial_3) = \left(\frac{1}{c}\frac{\partial}{\partial t}, \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) = \left(\frac{1}{c}\frac{\partial}{\partial t}, \boldsymbol{\nabla}\right). \tag{552}$$

It is easy to convince oneself of the nature of the indices in the above equation, because one has

$$\partial_\mu\, x^\nu = g^\nu_\mu. \tag{553}$$

Note that g^ν_μ with one upper and lower index, constructed via the metric tensor itself, $g^\nu_\mu = g_{\mu\rho}g^{\rho\nu}$ and is in essence a 'Kronecker delta', $g^0_0 = g^1_1 = g^2_2 = g^3_3 = 1$. The length squared of ∂ is the d'Alembertian operator, defined by

$$\Box \;=\; \partial^\mu\partial_\mu \;=\; \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \boldsymbol{\nabla}^2. \tag{554}$$

The value of the antisymmetric tensor $\epsilon^{\mu\nu\rho\sigma}$ is determined in the same way as for ϵ^{ijk}, starting from

$$\epsilon^{0123} = 1. \tag{555}$$

(Note that there are different conventions around and sometimes the opposite sign is used). It is an invariant tensor, not affected by Lorentz transformations. The product of two epsilon tensors is given by

$$\epsilon^{\mu\nu\rho\sigma}\epsilon^{\mu'\nu'\rho'\sigma'} = -\begin{vmatrix} g^{\mu\mu'} & g^{\mu\nu'} & g^{\mu\rho'} & g^{\mu\sigma'} \\ g^{\nu\mu'} & g^{\nu\nu'} & g^{\nu\rho'} & g^{\nu\sigma'} \\ g^{\rho\mu'} & g^{\rho\nu'} & g^{\rho\rho'} & g^{\rho\sigma'} \\ g^{\sigma\mu'} & g^{\sigma\nu'} & g^{\sigma\rho'} & g^{\sigma\sigma'} \end{vmatrix}, \tag{556}$$

$$\epsilon^{\mu\nu\rho\sigma}\epsilon_{\mu}{}^{\nu'\rho'\sigma'} = -\begin{vmatrix} g^{\nu\nu'} & g^{\nu\rho'} & g^{\nu\sigma'} \\ g^{\rho\nu'} & g^{\rho\rho'} & g^{\rho\sigma'} \\ g^{\sigma\nu'} & g^{\sigma\rho'} & g^{\sigma\sigma'} \end{vmatrix}, \tag{557}$$

$$\epsilon^{\mu\nu\rho\sigma}\epsilon_{\mu\nu}{}^{\rho'\sigma'} = -2\left(g^{\rho\rho'}\,g^{\sigma\sigma'} - g^{\rho\sigma'}\,g^{\sigma\rho'}\right), \tag{558}$$

$$\epsilon^{\mu\nu\rho\sigma}\epsilon_{\mu\nu\rho}{}^{\sigma'} = -6g^{\sigma\sigma'}, \tag{559}$$

$$\epsilon^{\mu\nu\rho\sigma}\epsilon_{\mu\nu\rho\sigma} = -24. \tag{560}$$

The first identity, for instance, is easily proven for $\epsilon^{0123}\,\epsilon^{0123}$ from which the general case can be obtained by making permutations of indices on the lefthandside and permutations of rows or columns on the righthandside. Each of these permutations leads to a minus sign, but more important has the same effect on lefthandside and righthandside. For the contraction of a vector with the antisymmetric tensor one often uses the shorthand notation

$$\epsilon^{ABCD} = \epsilon^{\mu\nu\rho\sigma}A_\mu B_\nu C_\rho D_\sigma. \tag{561}$$

C Exam questions 2012

Hand in at T224, T238 or mailbox of Mulders at latest on Thursday October 25, 2012

Exam exercise 1

In classical mechanics total energy, total momentum, total angular momentum and 'boosts' are conserved quantities (time-independent).

(a) How does one obtain these conserved quantities? Give the quantities for the free-moving CM system.

(b) What are the forms of the corresponding operators in quantum mechanics?

(c) Check the commutation relations of these quantities with the (free) Hamiltonian and discuss the time dependence of the expectation values.

Exam exercise 2

Consider the three-nucleon atomic nuclei ^{3}H (one proton, two neutrons) and ^{3}He (two protons, one neutron). In the groundstate the spatial part of the wave functions of protons and neutrons can (in first approximation) be taken as symmetric s-waves (in the relative coordinates).

(a) Construct the (spin part of the) wave function of these nuclei in terms of proton and neutron spin states, $|p\uparrow\rangle$, $|p\downarrow\rangle$, $|n\uparrow\rangle$ and $|n\downarrow\rangle$. You can best start with writing down the spin wave function for the two protons or two neutrons and then add the third nucleon.

(b) The magnetic moment of the nucleons is given by

$$\boldsymbol{\mu}_p = g_p \frac{e}{2M} \boldsymbol{s}_p \quad \text{and} \quad \boldsymbol{\mu}_n = g_n \frac{e}{2M} \boldsymbol{s}_n,$$

where M is the nucleon mass, $\boldsymbol{s}_p$ and s_n are the individual nucleon spin operators and $g_p \approx 5.6$ and $g_n \approx -3.8$. The magnetic moment operator of the nucleus is found as the sum of the nucleon magnetic moments,

$$\boldsymbol{\mu}_A = \sum_i g_i \frac{e}{2M} \boldsymbol{s}_i.$$

and can be written in terms of the total spin $\boldsymbol{S}$ (why? This is actually not a trivial question!),

$$\boldsymbol{\mu}_A = g \frac{e}{2M} \boldsymbol{S}.$$

Calculate g for ^{3}H and ^{3}He.

Exam exercise 3

We now go one level down and consider the three-quark description for protons p (two up quarks, one down quark) and n (two down quarks, one up quark). Again for the groundstate the orbital part of the wave functions of the quarks can be assumed to be s-waves. An important difference is that there is an additional degree of freedom, namely the color of the quarks. This color part of the wave function is a singlet wave function for three colors which is the completely antisymmetric combination,

$$|\text{color}\rangle = \frac{1}{\sqrt{6}} \left(|rgb\rangle - |grb\rangle + |gbr\rangle - |rbg\rangle + |brg\rangle - |bgr\rangle \right).$$

(a) Construct the (spin part of the) wave function of the nucleons, that have spin 1/2, in terms of quark spin states, $|u\uparrow\rangle$, $|u\downarrow\rangle$, $|d\uparrow\rangle$ and $|d\downarrow\rangle$. You can best start with writing down the spin wave functions for the two up quarks or two down quarks, respectively and then add the third quark (using appropriate Clebsch- Gordan coefficients).

(b) The sum of the magnetic moment operators of the quarks (being elementary fermions with g-factors being 2) are given by

$$\boldsymbol{\mu}_N = \sum_q g\,\frac{e_q}{2m_q}\,\boldsymbol{s}_q = \sum_q \frac{e_q}{m_q}\,\boldsymbol{s}_q,$$

where m_q is a quark (constituent) mass, which we as a first guess take to be $m_u = m_d = M/3$. The charges are $e_u = +2/3\,e$ and $e_d = -1/3\,e$. What do you find for the nucleon magnetic moments, i.e. calculate g_p and g_n in

$$\boldsymbol{\mu}_N = g_N\,\frac{e}{2M}\,\boldsymbol{s}_N.$$

(c) Show that it is possible to construct other three-quark spin states if all quarks remain in the (symmetric) lowest orbital wave function? What is the spin of this/these state(s) and give their wave function for that the state(s) that has/have two up quarks and one down quark.

Exam exercise 4

Look at the exact solution of a two-level problem where the unperturbed Hamiltonian H_0 has eigenvalues $E_1^{(0)}$ and $E_2^{(0)}$ and the perturbation is of the form

$$V = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}.$$

(a) Show in the limit that the matrix elements of V are much smaller than the difference of the unperturbed energies that the results for first and second order perturbation theory arise after expanding the exact results up to the appropriate order.

(b) Show that the diagonalization process also gives the new eigenstate and check that its expansion agrees with the result in perturbation theory (first order).

Exam Exercise 5

(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) Use the result to get the relativistic expression for the elastic Coulomb scattering cross section.

Exam exercise 6

(a) 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.

(b) 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 and the s-wave contribution to the cross section (consider what happens in the limit that V_0 becomes very strong or very weak).

Exam exercise 7

One can exactly solve the Klein-Gordon equation for stationary solutions with energy E in a central electric field. The solutions sre of the form

$$\psi(\boldsymbol{r},t) = \frac{u(r)}{r}\, Y_\ell^m(\theta,\varphi)\, e^{-iEt/\hbar},$$

Show that they satisfy

$$\left(E + \frac{Z\alpha\hbar c}{r}\right)^2 u(r) = \left(\hbar^2 c^2 \left(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2}\right) + m^2c^4\right) u(r). \tag{562}$$

By mapping this equation into a 'generalized Laguerre polynomial' form show that one finds solutions with energies

$$E_{n\ell} = \frac{mc^2}{\sqrt{1 + \frac{Z^2\alpha^2}{(n-\delta_\ell)^2}}}, \tag{563}$$

where $\delta_\ell = \ell + 1/2 - \sqrt{(\ell+1/2)^2 - Z^2\alpha^2}$.