Advanced Quantum Mechanics

P.J. Mulders

Department of Physics and Astronomy, Faculty of Sciences,
Vrije Universiteit Amsterdam
De Boelelaan 1081, 1081 HV Amsterdam, the Netherlands

email: mulders@few.vu.nl

September 2010 (vs 2.13)

vrije Universiteit amsterdam

Lectures given in the academic year 2010-2011

Voorwoord

The lectures Advanced Quantum Mechanics in the fall semester 2010 will be taught by Prof. Piet Mulders, assisted by Drs Wilco den Dunnen for the tutorial sessions.

We will be using various books, depending on the choice of topics. For the basis we will use the book *Introduction to Quantum Mechanics, second edition* van D.J. Griffiths (Pearson) or these lecture notes.

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 time.

Piet Mulders
September 2010

Schedule (indicative, to be completed later)

	Books	Notes	Exercises
Week 36	Griffiths 1 - 3, 5.3.2	1	1, 2, 3
	Griffiths 4.1 - 4.3	2, 3	
Week 37	Griffiths 4.4	4, 5	4, 5, 6
	CT X, p. 999-1058	4, 5	7, 8, 9, 10, 11, 12
Week 38	Griffiths 5.1, 5.2	6, 7	13, 14, 15
	Griffiths 6	8, 9	16, 17, 18, 19, 20
Week 39	Griffiths 7	10	21, 22
	Griffiths 9	11, 12	23
Week 40	Griffiths 10	13	24
Week 41			
Week 42			

Literature

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

Contents

1 Basics in quantum mechanics

1.1 Introduction

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 ($\psi \rightarrow \psi' = O\psi$). The position operator produces a new function by just multiplication with the position itself. The momentum operator acts as a derivative, $\boldsymbol{p} = -i\hbar\,\boldsymbol{\nabla}$, with the appropriate factors such that 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, for instance the *eigenstates* of any specific operator, given as a set of functions or more formal in the Dirac representation as quantum states $|\boldsymbol{r}\rangle$ or $|\boldsymbol{p}\rangle$, etc. Here the kets contain a set of 'good' quantum numbers, i.e. a number of eigenvalues of compatible (commuting) operators.

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

The coordinate state wave function then is nothing else as an 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 angular momentum operators $\ell_i = \epsilon_{ijk}\,r_j p_k$. The most important operator in quantum mechanics is the Hamiltonian. It determines the time evolution to be discussed below. The Hamiltonian $H(\boldsymbol{r},\boldsymbol{p},\boldsymbol{s})$ may also contain other operators corresponding to specific properties, such as the spin operators, satisfying the commutation relations

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

The 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 spin-space (a linear space over the complex numbers).

1.2 Translation symmetry

Symmetry considerations are at the heart of our understanding of nature. We have to understand how they are implemented in a quantum world. Let's start with translations as an example. Translations can be considered in space-time or in the Hilbert space of wave functions, it will affect operators, etc.

Let us start with translations in one dimension,

$$x \longrightarrow x' = x + a. \tag{3}$$

This is an example of a *continuous* transformation. There are many translations, in fact infinitely many determined by the continuous parameter a. Continuous transformations are contrasted with *discrete* transformations, such as $x \rightarrow x' = -x$ (space inversion, which is discussed elsewhere). One of the issues with transformations is the investigation of the consequences when it constitutes a symmetry transformation, i.e. when the 'world' is invariant under the transformation.

To see how we investigate the consequences referred to above, we first look at ways to 'translate a function' or 'translate an operator'. We first investigate what happens with a wave function. For continuous transformations, it turns out to be extremely useful to study first the infinitesimal problem (in general true for so-called Lie transformations). We get for small a a 'shifted' function

$$\phi'(x) = \phi(x+a) = \phi(x) + a\,\frac{d\phi}{dx} + \ldots = \underbrace{\left(1 + \frac{i}{\hbar}\,a\,p_x + \ldots\right)}_{U(a)}\phi(x), \tag{4}$$

which defines the shift operator $U(a)$ of which the momentum operator $p_x = -i\hbar\,(d/dx)$ is 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 (for operators new!) definition

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

one finds

$$U(a) = \exp\left(+\frac{i}{\hbar}\,a\,p_x\right). \tag{5}$$

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

How does a translation affect an operator? That is simple. Since we know that $O\phi$ is a function, we have

$$(O\phi)'(x) = O\phi(x+a) = U(a)O\phi(x) = \underbrace{U(a)OU^{-1}(a)}_{O'}\,\underbrace{U(a)\phi}_{\phi'}(x), \tag{6}$$

thus for operators

$$O \longrightarrow O' = U(a)\,O\,U^{-1}(a). \tag{7}$$

For continuous symmetries this implies for infinitesimal translations

$$O' = \left(1 + \frac{i}{\hbar}\,a\,p_x + \ldots\right) O \left(1 - \frac{i}{\hbar}\,a\,p_x + \ldots\right) = O + \frac{i}{\hbar}\,a\,[p_x, O] + \ldots. \tag{8}$$

This can be generalized to obtain a set of shifted operators $O(a)$ given by

$$O(a) = e^{i\,ap_x/\hbar}\,O(0)\,e^{-i\,ap_x/\hbar}, \tag{9}$$

for which one has

$$-i\hbar\,\frac{dO}{da} = e^{i\,ap_x/\hbar}\,\big[p_x, O\big]\,e^{-i\,ap_x/\hbar} \quad \text{and} \quad -\,i\hbar\,\left.\frac{dO}{da}\right|_{a=0} = \big[p_x, O\big]. \tag{10}$$

Exercise: Show that the above transformation properties for operators (for infinitesimal as well as for finite translations) imply for the position operators $x \to x' = x + a$, thus exactly the same behavior as for the 'coordinate' x. Show that the operator $p_x \to p_x' = p_x$.

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 $|x + a\rangle = U^{-1}(a)|x\rangle = U^\dagger(a)|x\rangle = e^{-i\,ap_x/\hbar}|x\rangle$.

Invariance under translations

Assume now that we have 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

$$H(x+a) = H(x) \iff [p_x, H] = 0. \tag{11}$$

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

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

Translation invariance can easily be generalized to three coordinates of one particle and to more particles by considering

$$\boldsymbol{r}_i \longrightarrow \boldsymbol{r}'_i = \boldsymbol{r}_i + \boldsymbol{a}. \tag{12}$$

The global shift operator is

$$U(\boldsymbol{a}) = \exp\left(+\boldsymbol{a}\cdot\sum_i \boldsymbol{\nabla}_i\right) = \exp\left(+\frac{i}{\hbar}\,\boldsymbol{a}\cdot\sum_i \boldsymbol{p}_i\right) = \exp\left(+\frac{i}{\hbar}\,\boldsymbol{a}\cdot\boldsymbol{P}\right), \tag{13}$$

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. 13

$$U(\boldsymbol{a})\,H\,U^{-1}(\boldsymbol{a}) = H \iff [\boldsymbol{P}, H] = 0. \tag{14}$$

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.

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 $U(d) = \exp(+i\,d\,p_x/\hbar)$,

$$[H, U(d)] = 0 \tag{15}$$

(prove this!). Thus these operators have a common set of eigenstates $\phi_{E,k}$, satisfying $H\,\phi_{E,k}(x) = E\,\phi_{E,k}(x)$ and $U(d)\,\phi_{E,k}(x) = e^{i\,kd}\,\phi_{E,k}(x)$ in which kd runs (for instance) between $-\pi \le kd \le \pi$. Using that $U(d)$ is the translation operator, one finds that

$$\phi_{E,k}(x+d) = e^{i\,kd}\,\phi_{E,k}(x) \tag{16}$$

Equivalently by writing ϕ as the *Bloch wave*

$$\phi_{E,k}(x) \equiv e^{ikx}\,u_{E,k}(x) \tag{17}$$

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 $d \rightarrow 0$)) the Bloch wave is constant and the wave function is a plain wave (with no restrictions on k, $-\infty < k < \infty$). 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).

1.3 Time evolution

In analogy to space translation, we have an (active) operator describing time evolution,

$$\psi'(t) = \psi(t+\tau) = \psi(t) + \tau\,\frac{d\psi}{dt} + \ldots = \underbrace{\left(1 - \frac{i}{\hbar}\,a\,H + \ldots\right)}_{U(\tau)}\psi(t). \tag{18}$$

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

$$U(\tau) = \exp\left(-\frac{i}{\hbar}\,\tau\,H\right). \tag{19}$$

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.

1.4 Rotational symmetry

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

$$\boldsymbol{r} \longrightarrow \boldsymbol{r}' = R(\hat{n},\alpha)\,\boldsymbol{r} \qquad \text{or} \qquad \varphi \longrightarrow \varphi' = \varphi + \alpha, \tag{20}$$

where the latter refers to the polar angle around the $\hat{n}$-direction, e.g. for a rotation around the z-axis one has explicitly

$$\left(\begin{array}{c} x \\ y \\ z \end{array}\right) \longrightarrow \left(\begin{array}{c} x' \\ y' \\ z' \end{array}\right) = \left(\begin{array}{ccc} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{array}\right)\left(\begin{array}{c} x \\ y \\ z \end{array}\right). \tag{21}$$

Note that here the components of the vector $\boldsymbol{r}$ change. It would correspond to a rotation $R(\hat{z}, -\alpha)$ for the axes. Such a rotation also gives rise to transformations in the Hilbert space of wave functions. Using polar coordinates and a rotation around the z-axis, we find

$$\phi(r,\theta,\varphi+\alpha) = \phi(r,\theta,\varphi) + \alpha\,\frac{\partial}{\partial\varphi}\,\phi + \ldots = \left(1 + \frac{i}{\hbar}\,\alpha\,\ell_z + \ldots\right)\phi, \tag{22}$$

from which one concludes that $\ell_z = -i\hbar(\partial/\partial\varphi)$ is the generator of rotations around the z-axis, and the rotation operator in the Hilbert space is

$$U(\hat{z},\alpha) = \exp\left(+\frac{i}{\hbar}\,\alpha\,\ell_z\right) = 1 + \frac{i}{\hbar}\,\alpha\,\ell_z + \ldots\ . \tag{23}$$

As for the translations, an operator (e.g. the Hamiltonian) behaves as

$$H(r,\theta,\varphi+\alpha) = H + \frac{i}{\hbar}\,\alpha\,[\ell_z, H] + \ldots = U(\hat{z},\alpha)\,H\,U^{-1}(\hat{z},\alpha). \tag{24}$$

$$= H(r,\theta,\varphi) + \alpha\left(\frac{\partial H}{\partial\varphi}\right) + \ldots \tag{25}$$

Rotational invariance (around z-axis) implies that

$$U(\hat{z},\alpha)\,H\,U^{-1}(\hat{z},\alpha) = H \iff [\boldsymbol{\ell}_z, H] = 0. \tag{26}$$

For more particles, invariance under rotations of the world implies

$$H \text{ invariant} \iff [\boldsymbol{L}, H] = 0, \tag{27}$$

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

Although the situation looks quite similar to the translations, there is an important difference. For two consecutive rotations the order is important (rotations do not commute). This is true 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 $U(\hat{x},\alpha)\,U(\hat{y},\beta) \neq U(\hat{y},\beta)\,U(\hat{x},\alpha)$. For the rotations in the Hilbert space, it is evident from the infinitesimal rotations. The generators (angular momentum operators) do not commute,

$$[\ell_i, \ell_j] = i\hbar\,\epsilon_{ijk}\,\ell_z.$$

Exercise: If you like a bit of puzzling, there is the Baker-Campbell-Hausdorff relation of which the first terms are

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

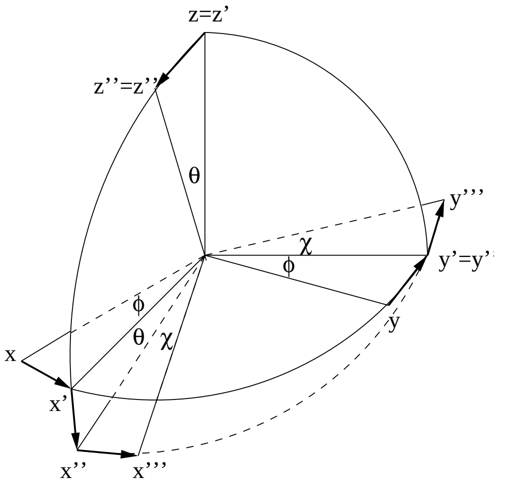
which shows that (only) for commuting operators one can 'add' the operators in the exponent, as is known to work for numbers.

Positions and momenta are not invariant under rotations. Quantummechanically this translates into the non-commutativity of the generators of rotations $\boldsymbol{\ell}$ and these operators. The commutation relations

$$[\ell_i, r_j] = i\hbar\,\epsilon_{ijk}\,r_k, \tag{28}$$

$$[\ell_i, p_j] = i\hbar\,\epsilon_{ijk}\,p_k, \tag{29}$$

just imply for operators $\boldsymbol{r} \rightarrow \boldsymbol{r}' = R(\hat{n},\alpha)\boldsymbol{r}$ and $\boldsymbol{p} \rightarrow \boldsymbol{p}' = R(\hat{n},\alpha)\boldsymbol{p}$, i.e. the same behavior as the coordinate $\boldsymbol{r}$ and the same as classical positions and momenta.



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

$$U_E(\varphi,\theta,\chi) = e^{-i\varphi\,\ell_z/\hbar}\,e^{-i\theta\,\ell_y/\hbar}\,e^{-i\chi\,\ell_z/\hbar}. \tag{30}$$

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.

1.5 Gallilean invariance

From classical mechanics we know that there are a number of basic symmetries governing the physical world, known as the (ten) Gallilean transformations. These are

$$\begin{aligned}
t &\rightarrow t' = t + \tau, && \text{one time translation,} && (31)\\
\boldsymbol{r} &\rightarrow \boldsymbol{r}' = \boldsymbol{r} + \boldsymbol{a} && \text{three translations,} && (32)\\
\boldsymbol{r} &\rightarrow \boldsymbol{r}' = R(\hat{n}, \alpha)\boldsymbol{r} && \text{three rotations,} && (33)\\
\boldsymbol{r} &\rightarrow \boldsymbol{r}' = \boldsymbol{r} - \boldsymbol{u}t && \text{three boosts.} && (34)
\end{aligned}$$

Classically one can show that invariance under these transformations implies conserved quantities, for time translations the total *energy* E, for space translations the total *momentum* $\boldsymbol{P}$, for rotations the total *angular momentum* $\boldsymbol{L}$. Also boost invariance implies a conserved quantity, namely $\boldsymbol{K} = M\boldsymbol{R} - t\boldsymbol{P}$. Boost invariance will become much more important when we later consider the transformations in a relativistic theory (Lorentz invariance instead of Gallilean invariance).

In quantum mechanics, the conserved quantities correspond to operators of which the expectation value is time independent. These are precisely the generators of the corresponding symmetries. From the known relation

$$i\hbar\,\frac{d\langle O\rangle}{dt} = [H, O] + \langle\frac{\partial O}{\partial t}\rangle. \tag{35}$$

one sees that this is true if $[H, P_i] = [H, L_i] = 0$ and $[H, K_i] = -i\hbar\,P_i$. These specific commutators are part of the full set of commutation relations between the 10 generators of the Gallilei group (known as the Lie algebra),

$$\begin{aligned}
&[P_i, P_j] = [P_i, H] = [J_i, H] = 0,\\
&[J_i, J_j] = i\hbar\,\epsilon_{ijk} J_k, \quad [J_i, P_j] = i\hbar\,\epsilon_{ijk} P_k, \quad [J_i, K_j] = i\hbar\,\epsilon_{ijk} K_k,\\
&[K_i, H] = i\hbar\,P_i, \quad [K_i, K_j] = 0, \quad [K_i, P_j] = 0.
\end{aligned} \tag{36}$$

For the generators of the rotations we have used here $\boldsymbol{J}$ instead of $\boldsymbol{L}$, because, as we shall shortly see, the full rotation matrix can and even has to be more than just the orbital angular momentum, including an intrinsic angular momentum (spin). The second line in this equation simply gives the characteristic behavior of *vectors* under rotations.

It is easy to check that for a single (free) particle the quantum mechanical set of operators

$$\begin{aligned}
H &= \frac{\boldsymbol{p}^2}{2M}, && (37)\\
\boldsymbol{P} &= \boldsymbol{p}, && (38)\\
\boldsymbol{J} &= \boldsymbol{\ell} + \boldsymbol{s} = \boldsymbol{r} \times \boldsymbol{p} + \boldsymbol{s} && (39)\\
\boldsymbol{K} &= m\boldsymbol{r} - t\boldsymbol{p}. && (40)
\end{aligned}$$

satisfy the above commutation relations (do this!), starting with the *canonical* relations $[r_i, p_j] = i\hbar\,\delta_{ij}$ and for spin operators $[s_i, s_j] = i\hbar\,\epsilon_{ijk}\,s_k$ and $[r_i, s_j] = [p_i, s_j] = 0$. The latter two commutators imply that spin decouples from the spatial part of the wave function.

Adding a potential $V(\boldsymbol{r})$ to the Hamiltonian, the commutation relations would no longer indicate Gallilei invariance. A potential (e.g. centered around an origin) breaks translation invariance, the specific

$\boldsymbol{r}$-dependence might break rotational invariance, etc. On the other hand, for two particles one finds that in terms of CM and relative coordinates using total and reduced masses $M = m_1 + m_2$ and $\mu = m_1\, m_2/M$ the generators

$$\begin{aligned} H &= H_1 + H_2 = \frac{\boldsymbol{P}^2}{2M} + H_{\text{int}}, \\ \boldsymbol{P} &= \boldsymbol{P}_1 + \boldsymbol{P}_2 = \boldsymbol{P}, \\ \boldsymbol{J} &= \boldsymbol{\ell}_1 + \boldsymbol{s}_1 + \boldsymbol{\ell}_2 + \boldsymbol{s}_2 = \boldsymbol{R} \times \boldsymbol{P} + \boldsymbol{S}, \\ \boldsymbol{K} &= \boldsymbol{K}_1 + \boldsymbol{K}_2 = M\,\boldsymbol{R} - t\,\boldsymbol{P}, \end{aligned} \tag{41}$$

satisfy the commutation relations for the Gallilei group, where

$$\begin{aligned} &\boldsymbol{P} = \boldsymbol{p}_1 + \boldsymbol{p}_2 \quad \text{and} \quad \boldsymbol{p} = \frac{m_2}{M}\,\boldsymbol{p}_1 - \frac{m_1}{M}\,\boldsymbol{p}_2, \\ &\boldsymbol{R} = \frac{m_1}{M}\,\boldsymbol{r}_1 + \frac{m_2}{M}\,\boldsymbol{r}_2 \quad \text{and} \quad \boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2, \\ &\boldsymbol{S} = \boldsymbol{r} \times \boldsymbol{p} + \boldsymbol{s}_1 + \boldsymbol{s}_2, \\ &H_{int} = \frac{\boldsymbol{p}^2}{2\mu} + V(\boldsymbol{r}, \boldsymbol{p}, \boldsymbol{s}_1, \boldsymbol{s}_2). \end{aligned}$$

All commutation relations start simply from the canonical commutation relation 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.*

Finally we note that in classical mechanics the Lie algebra structure of the symmetry group is evident in the Poisson bracket structure of particular quantities A and B, which in that case are functions of positions and momenta,

$$[A(x,p), B(x,p)]_P \equiv \frac{dA}{dx}\,\frac{dB}{dp} - \frac{dA}{dp}\,\frac{dB}{dx}.$$

Exercise: In analogy to Eq. 10 one has for the generators of boost transformations,

$$-i\hbar\,\left.\frac{dO}{du_x}\right|_{u_x=0} = \big[K_x, O\big], \text{ etc.}$$

Use this relation to derive $[K_i, r_j]$ and $[K_i, p_j]$ from the requirement that the classical behavior $\boldsymbol{r} \rightarrow \boldsymbol{r}' = \boldsymbol{r} - \boldsymbol{u}t$ and $\boldsymbol{p} \rightarrow \boldsymbol{p}' = \boldsymbol{p} - m\boldsymbol{u}$ remains valid for the operators. Check that these commutation relations are satisfied for $\boldsymbol{K} = m\boldsymbol{r} - t\boldsymbol{p}$.

Exercise: Check that the canonical 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 $\boldsymbol{p}$.

Exercise: Check that

$$\boldsymbol{\ell}_1 + \boldsymbol{\ell}_2 = \boldsymbol{r}_1 \times \boldsymbol{p}_1 + \boldsymbol{r}_2 \times \boldsymbol{p}_2 = \boldsymbol{R} \times \boldsymbol{P} + \boldsymbol{r} \times \boldsymbol{p}.$$

1.6 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,

$$\boldsymbol{r} \longrightarrow -\boldsymbol{r} \qquad \text{and} \qquad t \longrightarrow t, \tag{42}$$

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

$$\boldsymbol{p} \longrightarrow -\boldsymbol{p} \qquad \text{and} \qquad \boldsymbol{\ell} \longrightarrow \boldsymbol{\ell}. \tag{43}$$

The same is true for the 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

$$P\phi(\boldsymbol{r}) \equiv \phi(-\boldsymbol{r}). \tag{44}$$

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,

$$P\phi_\pi(\boldsymbol{r}) = \pi\,\phi_\pi(\boldsymbol{r}), \tag{45}$$

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: Although this looks evident, think carefully about the proof, which requires comparing $P^2\phi$ using Eqs 44 and 45.

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

$$A\phi \longrightarrow PA\phi = \underbrace{PAP^{-1}}_{A'}\,\underbrace{P\phi}_{\phi'}, \quad \text{thus} \quad A \longrightarrow PAP^{-1}. \tag{46}$$

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

$$\boldsymbol{r} \longrightarrow P\boldsymbol{r}P^{-1} = -\hat{\boldsymbol{r}}, \tag{47}$$
$$\boldsymbol{p} \longrightarrow P\boldsymbol{p}P^{-1} = -\hat{\boldsymbol{p}}, \tag{48}$$
$$\boldsymbol{\ell} \longrightarrow P\boldsymbol{\ell}P^{-1} = +\hat{\boldsymbol{\ell}}, \tag{49}$$
$$H(\boldsymbol{r}, \boldsymbol{p}) \longrightarrow PH(\boldsymbol{r}, \boldsymbol{p})P^{-1} = H(-\boldsymbol{r}, -\boldsymbol{p}). \tag{50}$$

If H is invariant under inversion, one has

$$PHP^{-1} = H \quad \Longleftrightarrow \quad [P, H] = 0. \tag{51}$$

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 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 $\{P, O\} = PO + OP = 0$).

1.7 Time reversal

In classical mechanics with second order differential equations, one has for time-independent forces automatically time reversal invariance, i.e. invariance under $t \rightarrow -t$ and $\boldsymbol{r} \rightarrow \boldsymbol{r}$. 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 $\boldsymbol{\nabla} \rightarrow \boldsymbol{\nabla}$. Similarly one has classically $E \rightarrow E$, 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 $\boldsymbol{p} = -i\hbar\boldsymbol{\nabla} \rightarrow i\hbar\boldsymbol{\nabla} = -\boldsymbol{p}$ and $H \rightarrow H$. 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

$$T|\phi\rangle = \langle T\phi|, \tag{52}$$

which for matrix elements implies

$$\langle\phi|\psi\rangle = \langle\phi|T^\dagger T|\psi\rangle = \langle T\psi|T\phi\rangle = \langle T\phi|T\psi\rangle^* \tag{53}$$

$$\langle\phi|A|\psi\rangle = \langle\phi|T^\dagger T\,A\,T^\dagger T|\psi\rangle = \langle T\phi|A|T\psi\rangle^*. \tag{54}$$

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.

2 Angular momentum and spherical harmonics

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

$$x = r\,\sin\theta\,\cos\varphi, \tag{55}$$

$$y = r\,\sin\theta\,\sin\varphi, \tag{56}$$

$$z = r\,\cos\theta, \tag{57}$$

from which one gets

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

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

$$\hat{\ell}_x = -i\hbar\left(y\,\frac{\partial}{\partial z} - z\,\frac{\partial}{\partial y}\right) = i\hbar\left(\sin\varphi\,\frac{\partial}{\partial\theta} + \cot\theta\,\cos\varphi\,\frac{\partial}{\partial\varphi}\right), \tag{58}$$

$$\hat{\ell}_y = -i\hbar\left(z\,\frac{\partial}{\partial x} - x\,\frac{\partial}{\partial z}\right) = i\hbar\left(-\cos\varphi\,\frac{\partial}{\partial\theta} + \cot\theta\,\sin\varphi\,\frac{\partial}{\partial\varphi}\right), \tag{59}$$

$$\hat{\ell}_z = -i\hbar\left(x\,\frac{\partial}{\partial y} - y\,\frac{\partial}{\partial x}\right) = -i\hbar\,\frac{\partial}{\partial\varphi}, \tag{60}$$

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

$$\hat{\ell}^2 = \ell_x^2 + \ell_y^2 + \ell_z^2 = -\hbar^2\left[\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2}\right]. \tag{61}$$

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

2.1 Spherical harmonics

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

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

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

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

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

Using polar coordinates one easily sees that 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 eigenfunctions of $\boldsymbol{\ell}^2$ and ℓ_z, referred to as the spherical harmonics, are given by

$$\hat{\ell}^2\,Y_\ell^m(\theta,\varphi) = \ell(\ell+1)\hbar^2\,Y_\ell^m(\theta,\varphi), \tag{62}$$

$$\hat{\ell}_z\,Y_\ell^m(\theta,\varphi) = m\hbar\,Y_\ell^m(\theta,\varphi), \tag{63}$$

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

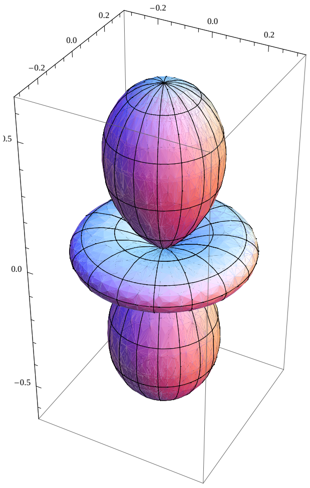
$$Y_0^0(\theta,\varphi) = \frac{1}{\sqrt{4\pi}}. \tag{64}$$

Explicit results for $\ell = 1$ are

$$Y_1^1(\theta,\varphi) = -\sqrt{\frac{3}{8\pi}}\,\frac{x+iy}{r} = -\sqrt{\frac{3}{8\pi}}\,\sin\theta\,e^{i\varphi}, \tag{65}$$

$$Y_1^0(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\,\frac{z}{r} = \sqrt{\frac{3}{4\pi}}\,\cos\,\theta, \tag{66}$$

$$Y_1^{-1}(\theta,\varphi) = \sqrt{\frac{3}{8\pi}}\,\frac{x-iy}{r} = \sqrt{\frac{3}{8\pi}}\,\sin\theta\,e^{-i\varphi}. \tag{67}$$



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

$$Y_2^{\pm 2}(\theta,\varphi) = \sqrt{\frac{15}{32\pi}}\,\frac{(x^2-y^2) \pm 2i\,xy}{r^2} = \sqrt{\frac{15}{32\pi}}\,\sin^2\theta\,e^{\pm 2i\varphi}, \tag{68}$$

$$Y_2^{\pm 1}(\theta,\varphi) = \mp\sqrt{\frac{15}{8\pi}}\,\frac{z(x \pm iy)}{r^2} = \mp\sqrt{\frac{15}{8\pi}}\,\sin\theta\,\cos\,\theta\,e^{\pm i\varphi}. \tag{69}$$

$$Y_2^0(\theta,\varphi) = \sqrt{\frac{5}{16\pi}}\,\frac{3\,z^2-r^2}{r^2} = \sqrt{\frac{5}{16\pi}}\,\left(3\cos^2\theta - 1\right), \tag{70}$$

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

$$\int d\Omega\; Y_\ell^{m*}(\theta,\varphi)\, Y_{\ell'}^{m'}(\theta,\varphi) = \delta_{\ell\ell'}\,\delta_{mm'}. \tag{71}$$

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,

$$Y_\ell^m(\theta,\varphi) = (-)^{(m+|m|)/2}\sqrt{\frac{2\ell+1}{4\pi}\,\frac{(\ell-|m|)!}{(\ell+|m|)!}}\,P_\ell^{|m|}(\cos\,\theta)\,e^{im\varphi}, \tag{72}$$

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

$$P_\ell^{|m|}(x) = \frac{1}{2^\ell\,\ell!}\,(1-x^2)^{|m|/2}\,\frac{d^{\ell+|m|}}{dx^{\ell+|m|}}\,\left[(x^2-1)^\ell\right]. \tag{73}$$

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

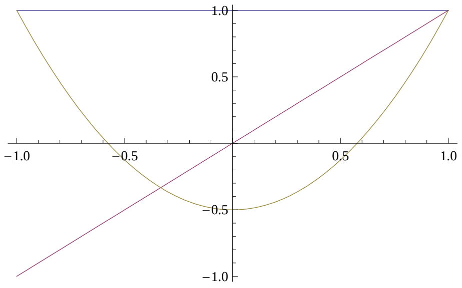
$$P_\ell(\cos\,\theta) = \sqrt{\frac{4\pi}{2\ell+1}}\,Y_\ell^0(\theta). \tag{74}$$

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

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

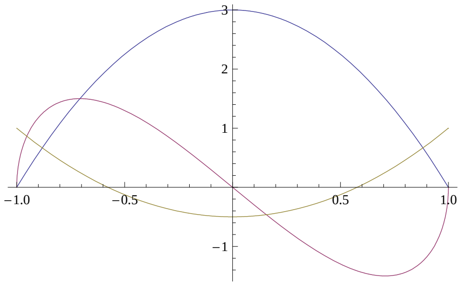
(given in the figure to the right).



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).



2.2 The radial Schrödinger equation

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

$$H\,\psi(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\boldsymbol{r})\right]\psi(\boldsymbol{r}) = E\,\psi(\boldsymbol{r}). \tag{75}$$

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

$$\begin{aligned}
\boldsymbol{\nabla}^2 &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\,\frac{\partial}{\partial r}\right) + \frac{1}{r^2\,\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\,\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2} && (76)\\
&= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\,\frac{\partial}{\partial r}\right) - \frac{\boldsymbol{\ell}^2}{\hbar^2\,r^2}. && (77)
\end{aligned}$$

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

$$\psi_{n\ell m}(\boldsymbol{r}) = R_{n\ell m}(r)\,Y_\ell^m(\theta,\varphi). \tag{78}$$

Inserting this in the eigenvalue equation one obtains

$$\left[-\frac{\hbar^2}{2m\,r^2}\frac{\partial}{\partial r}\left(r^2\,\frac{\partial}{\partial r}\right) + \left(\frac{\hbar^2\,\ell(\ell+1)}{2m\,r^2} + V(r)\right)\right] R_{n\ell}(r) = E_{n\ell}\,R_{n\ell}(r), \tag{79}$$

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

$$\psi(\boldsymbol{r}) = R(r)\,Y_\ell^m(\theta,\varphi) = \frac{u(r)}{r}\,Y_\ell^m(\theta,\varphi). \tag{80}$$

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

$$\left[-\frac{\hbar^2}{2m}\,\frac{d^2}{dr^2} + \underbrace{\frac{\hbar^2\,\ell(\ell+1)}{2m\,r^2} + V(r)}_{V_{\rm eff}(r)} - E_{n\ell}\right] u_{n\ell}(r) = 0, \tag{81}$$

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

$$\int d^3r\;\psi_1^*(\boldsymbol{r})\,O\,\psi_2(\boldsymbol{r}) = \int_0^\infty r^2\,dr\int d\Omega\;\psi_1^*(\boldsymbol{r})\,O\,\psi_2(\boldsymbol{r}) = \int_0^\infty dr\;u_1^*(r)\,O\,u_2(r).$$

---

[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.

2.3 The free wave solution

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 of the homogeneous where the radial wave function $u(r)$ satisfies the homogeneous equation

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k^2\right) u_\ell(r) = 0, \tag{82}$$

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:

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

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

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

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

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

Having two equivalent ways of solving the free Schrödinger equation, it must be possible to express the plane wave as an expansion into these spherical solutions. This expansion is

$$\exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) = e^{i\,kz} = e^{i\,kr\,\cos\theta} = \sum_{\ell=0}^{\infty}(2\ell+1)\,i^\ell\,j_\ell(kr)\,P_\ell(\cos\theta), \tag{83}$$

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

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 $x_{n0} = n\pi$, $x_{11} = 4.493$, $x_{21} = 7.725$, $x_{12} = 5.763$, $x_{22} = 9.095$, $x_{13} = 6.988$, $x_{14} = 8.183$, $x_{15} = 9.356$.

---

3 The hydrogen atom

3.1 Transformation to the center of mass

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

$$H = -\frac{\hbar^2}{2m_N}\boldsymbol{\nabla}_p^2 - \frac{\hbar^2}{2m_e}\boldsymbol{\nabla}_e^2 - \frac{Ze^2}{4\pi\epsilon_0\,|\boldsymbol{r}_e - \boldsymbol{r}_p|}. \tag{84}$$

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

$$M\boldsymbol{R} = m_N\boldsymbol{r}_N + m_e\boldsymbol{r}_e \quad \text{and} \quad \boldsymbol{r} = \boldsymbol{r}_e - \boldsymbol{r}_N, \tag{85}$$

and similar momenta

$$\boldsymbol{P} = \boldsymbol{p}_e + \boldsymbol{p}_N = -i\hbar\boldsymbol{\nabla}_R, \quad \text{and} \quad \frac{\boldsymbol{p}}{m} = \frac{\boldsymbol{p}_e}{m_e} - \frac{\boldsymbol{p}_N}{m_N} = -\frac{i\hbar}{m}\boldsymbol{\nabla}_r. \tag{86}$$

One obtains

$$H = \underbrace{-\frac{\hbar^2}{2M}\boldsymbol{\nabla}_R^2}_{H_{\rm cm}} \underbrace{-\frac{\hbar^2}{2m}\boldsymbol{\nabla}_r^2 - \frac{Ze^2}{4\pi\epsilon_0\,r}}_{H_{\rm rel}}. \tag{87}$$

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

3.2 Solving the eigenvalue equation

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

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \underbrace{\frac{\hbar^2\,\ell(\ell+1)}{2m\,r^2} + V_c(r)}_{V_{\rm eff}(r)} - E\right]u_{n\ell}(r) = 0, \tag{88}$$

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

$$\left[-\frac{d^2}{d\rho^2} + \frac{\ell(\ell+1)}{\rho^2} - \frac{e^2}{4\pi\epsilon_0}\,\frac{2m\,a_0}{\hbar^2}\,\frac{Z}{\rho} - \frac{2m\,a_0^2\,E}{\hbar^2}\right]u_{E\ell}(\rho) = 0. \tag{89}$$

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

$$a_0 \equiv \frac{4\pi\epsilon_0\,\hbar^2}{m\,e^2}. \tag{90}$$

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

$$R_\infty = \frac{\hbar^2}{2m\,a_0^2} = \frac{1}{2}\,\frac{e^2}{4\pi\epsilon_0\,a_0} = \frac{m\,e^4}{32\pi^2\epsilon_0^2\,\hbar^2}. \tag{91}$$

One then obtains the dimensionless equation

$$\left[-\frac{d^2}{d\rho^2}+\frac{\ell(\ell+1)}{\rho^2}-\frac{2Z}{\rho}-\epsilon\right]u_{\epsilon\ell}(\rho)=0 \tag{92}$$

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

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

$$\alpha = \frac{e^2}{4\pi\,\epsilon_0\,\hbar c} \approx 1/137, \tag{93}$$

$$a_0 \equiv \frac{4\pi\epsilon_0\,\hbar^2}{m\,e^2} = \frac{4\pi\epsilon_0\,\hbar c}{e^2}\,\frac{\hbar c}{mc^2} = \frac{1}{\alpha}\,\frac{\hbar c}{mc^2} \approx 0.53\times 10^{-10}\ \mathrm{m}, \tag{94}$$

$$R_\infty = \frac{\hbar^2}{2m\,a_0^2} = \frac{1}{2}\,\alpha\left(\frac{\hbar c}{a_0}\right) = \frac{1}{2}\,\alpha^2\,mc^2 \approx 13.6\ \mathrm{eV}. \tag{95}$$

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

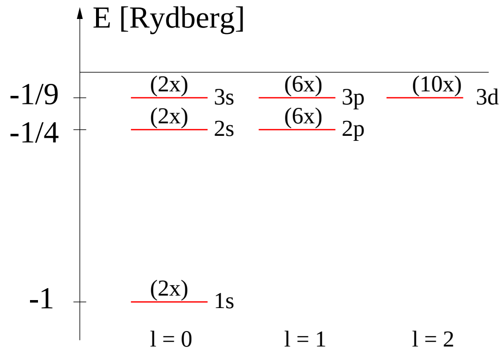
To find the solutions in general, we can turn to an algebraic manipulation program or a mathematical handbook to look for the solutions of the dimensionless differential equation (see subsection on Laguerre polynomials). We see from this treatment that (using $p \to n-\ell-1$, $a \to 2\ell+1$ and $x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

$$u_{n\ell}(\rho) = \left(\frac{2Z}{n\,a_0}\right)^{1/2}\sqrt{\frac{(n-\ell-1)!}{2n\,(n+\ell)!}}\;e^{-Z\rho/n}\left(\frac{2Z\rho}{n}\right)^{\ell+1}L^{2\ell+1}_{n-\ell-1}\left(\frac{2Z\rho}{n}\right) \tag{96}$$

with eigenvalues (energies)

$$E_{n\ell} = -\frac{Z^2}{n^2}\,R_\infty, \tag{97}$$

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



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

Some aspects of the solution can be easily understood. For instance, looking at equation 92 one sees that the asymptotic behavior of the wave function is found from

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

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

Explicitly, the lowest solutions are:

$$u_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/a_0}\left(\frac{Zr}{a_0}\right), \tag{98}$$

$$u_{20}(r) = \frac{1}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/2a_0}\left(\frac{Zr}{a_0}\right)\left(1-\frac{1}{2}\frac{Zr}{a_0}\right) \tag{99}$$

$$u_{21}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/2a_0}\left(\frac{Zr}{a_0}\right)^2 \tag{100}$$

$$u_{30}(r) = \frac{2}{3\sqrt{3}}\left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/3a_0}\left(\frac{Zr}{a_0}\right)\left(1-\frac{2}{3}\frac{Zr}{a_0}+\frac{2}{27}\left(\frac{Zr}{a_0}\right)^2\right) \tag{101}$$

$$u_{31}(r) = \frac{8}{27\sqrt{6}}\left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/3a_0}\left(\frac{Zr}{a_0}\right)^2\left(1-\frac{1}{6}\frac{Zr}{a_0}\right) \tag{102}$$

$$u_{32}(r) = \frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/3a_0}\left(\frac{Zr}{a_0}\right)^3 \tag{103}$$

Useful integrals involving the solutions are expectation values like

$$\langle\frac{r^2}{a_0^2}\rangle = \frac{n^2}{2Z^2}\left[5n^2 - 3\,\ell(\ell+1)+1\right], \tag{104}$$

$$\langle\frac{r}{a_0}\rangle = \frac{1}{2Z}\left[3\,n^2 - \ell(\ell+1)\right], \tag{105}$$

$$\langle\frac{a_0}{r}\rangle = \frac{Z}{n^2}, \tag{106}$$

$$\langle\frac{a_0^2}{r^2}\rangle = \frac{2\,Z^2}{n^3(2\ell+1)}, \tag{107}$$

$$\langle\frac{a_0^3}{r^3}\rangle = \frac{2\,Z^3}{n^3\,\ell(\ell+1)(2\ell+1)}. \tag{108}$$

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.

3.3 Appendix: Generalized Laguerre polynomials

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

$$y'' + g_0(x)\,y = 0 \qquad \text{with} \quad g_0(x) = \left[\frac{2p+a+1}{2x} + \frac{1-a^2}{4x^2} - \frac{1}{4}\right], \tag{109}$$

are given by

$$y(x) = e^{-x/2}\,x^{(a+1)/2}\,L_p^a(x). \tag{110}$$

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

$$\int_0^\infty dx\; x^{a+1}\,e^{-x}\;\left[L_p^a(x)\right]^2 = (2p+a+1)\,\frac{(p+a)!}{p!}, \tag{111}$$

and also satisfy the differential equation

$$\left[x\,\frac{d^2}{dx^2} + (a+1-x)\,\frac{d}{dx} + p\right] L_p^a(x) = 0. \tag{112}$$

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

$$L_p(x) \equiv L_p^0(x) = \frac{e^x}{p!}\,\frac{d^p}{dx^p}\left[x^p\,e^{-x}\right] = \frac{1}{p!}\left(\frac{d}{dx} - 1\right)^p x^p, \tag{113}$$

$$L_p^a(x) = (-)^a\,\frac{d^a}{dx^a}\left[L_{p+a}(x)\right]. \tag{114}$$

Some general expressions are

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

Some recursion relations are

$$(p+1)\,L_{p+1}^a(x) = (2p+a+1-x)\,L_p^a(x) - (p+a)\,L_{p-1}^a(x), \tag{115}$$

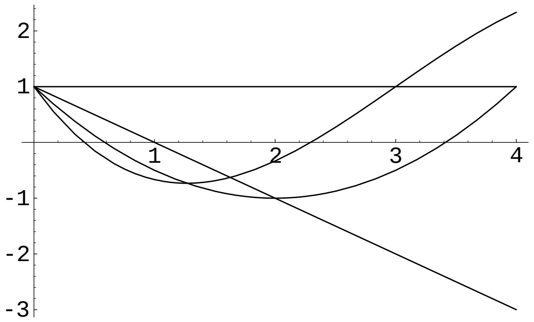
$$x\,L_p^{a+1}(x) = (x-p)\,L_p^a(x) + (p+a)\,L_{p-1}^a(x), \tag{116}$$

$$L_p^a(x) = L_p^{a-1}(x) + L_{p-1}^a(x). \tag{117}$$

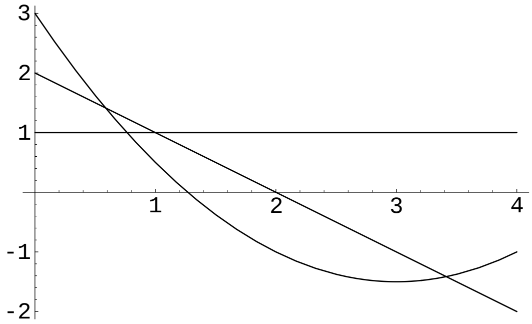
Some explicit polynomials are

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

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



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.

3.4 A note on Bohr quantization

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

$$\frac{mv^2}{r} = \frac{Z\,e^2}{4\pi\epsilon_0\,r^2}, \tag{118}$$

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

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

Using the quantization condition on ℓ to eliminate v one finds

$$r_n = \frac{n^2}{Z}\,\frac{4\pi\epsilon_0\,\hbar^2}{m\,e^2}, \tag{119}$$

$$E_n = \frac{Z^2}{n^2}\,\frac{m\,e^4}{32\pi\epsilon_0^2\hbar^2}, \tag{120}$$

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

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

4 Spin

4.1 Definition

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

$$[s_i, s_j] = i\hbar\epsilon_{ijk}\, s_k, \tag{121}$$

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.

4.2 Rotation invariance

For the orbital angular momentum, we have seen the link to 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

$$\left.\begin{array}{l}[\ell_i, S] = 0\\ [\ell_i, V_j] = i\hbar\,\epsilon_{ijk}\, V_k\end{array}\right\}\ \text{for a single particle without spin,} \tag{122}$$

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 seems 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

$$\boldsymbol{j} \equiv \boldsymbol{\ell} + \boldsymbol{s}, \tag{123}$$

we do get

$$\left.\begin{array}{l}[j_i, S] = 0\\ [j_i, V_j] = i\hbar\,\epsilon_{ijk}\, V_k,\end{array}\right\}\ \text{for a single particle} \tag{124}$$

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

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

$$\boldsymbol{L} = \sum_{n=1}^{N} \boldsymbol{\ell}_n, \qquad \boldsymbol{S} = \sum_{n=1}^{N} \boldsymbol{s}_n, \qquad \boldsymbol{J} = \sum_{n=1}^{N} \boldsymbol{j}_n = \boldsymbol{L} + \boldsymbol{S}, \tag{125}$$

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

$$\left.\begin{array}{l}[J_i, S] = 0\\ [J_i, V_j] = i\hbar\,\epsilon_{ijk}\, V_k\end{array}\right\}\ \text{for an isolated system} \tag{126}$$

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

Exercise: Show that the inner product $\boldsymbol{a}\cdot\boldsymbol{b}$ of two vector operators satisfying the commutation relation in Eq. 126 indeed behaves as a scalar operator, satifying the required scalar commutation relation.

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

$$[\boldsymbol{J}, H] = 0, \tag{127}$$

where $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S} = \sum_i (\boldsymbol{\ell}_i + \boldsymbol{s}_i)$. This is the (generalized, cf. Eq. 27) 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 $\boldsymbol{\ell}$.

4.3 Spin states

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

$$[s_i, s_j] = i\hbar\,\epsilon_{ijk}\,s_k, \tag{128}$$

$$[\boldsymbol{s}^2, s_i] = 0. \tag{129}$$

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

$$\boldsymbol{s}^2|s,m\rangle = \hbar^2\,s(s+1)|s,m\rangle, \tag{130}$$

$$\boldsymbol{s}_z|s,m\rangle = m\hbar\,|s,m\rangle. \tag{131}$$

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

$$s_\pm \equiv s_x \pm i\,s_y. \tag{132}$$

The commutation relations for these operators are,

$$[\boldsymbol{s}^2, s_\pm] = 0, \tag{133}$$

$$[s_z, s_\pm] = \pm\hbar\,s_\pm, \tag{134}$$

$$[s_+, s_-] = 2\hbar\,s_z, \tag{135}$$

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

$$\begin{aligned}
s_+|s,m\rangle &= \hbar\sqrt{s(s+1)-m(m+1)}\,|s,m+1\rangle\\
&= =\hbar\sqrt{(s-m)(s+m+1)}\,|s,m+1\rangle \qquad (136)\\
s_-|s,m\rangle &= \hbar\sqrt{s(s+1)-m(m-1)}\,|s,m-1\rangle\\
&= \hbar\sqrt{(s+m)(s-m+1)}\,|s,m-1\rangle. \qquad (137)
\end{aligned}$$

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 136 and 137 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.

4.4 Why is ℓ integer

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

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

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

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

4.5 Matrix representations of spin operators

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

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

Using the definition of the quantum numbers in Eq. 131 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

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

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.

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

4.6 Rotated spin states

Instead of the spin states defined as eigenstates of s_z, one might be interested in eigenstates of $\boldsymbol{s} \cdot \hat{\boldsymbol{n}}$, e.g. because one wants to measure it with a Stern-Gerlach apparatus with an inhomogeneous $\boldsymbol{B}$-field in the $\hat{\boldsymbol{n}}$ direction. We choose an appropriate notation like $|\hat{\boldsymbol{n}}, \pm\rangle$ or two component spinors $\chi^{(s)}_{m_s}(\hat{\boldsymbol{n}})$, shorthand

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

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

$$\boldsymbol{s}\cdot\hat{\boldsymbol{n}} = \frac{1}{2}\,\hbar\,\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}} = \frac{\hbar}{2}\left(\begin{array}{cc} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{array}\right). \tag{138}$$

We find the following two eigenstates and eigenvalues

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

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,

$$U(\theta, \hat{\boldsymbol{n}}) = \exp\left(i\,\theta\,\hat{\boldsymbol{n}}\cdot\boldsymbol{J}\right), \tag{139}$$

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,

$$\langle j, m'|U(\varphi, \theta, -\varphi)|j, m\rangle = D^{(j)}_{m'm}(\varphi, \theta, -\varphi) = e^{i(m-m')\varphi}\,d^{(j)}_{m'm}(\theta). \tag{140}$$

In general the rotated eigenstates are written as

$$\chi^{(s)}_m(\hat{\boldsymbol{n}}) \;=\; \left(\begin{array}{c} d^{(s)}_{sm}(\theta) \\ \vdots \\ d^{(s)}_{m'm}(\theta) \\ \vdots \\ d^{(s)}_{-sm}(\theta) \end{array}\right). \tag{141}$$

---

[2] Use the relation $\exp\left(i\theta\,\hat{\boldsymbol{n}}\cdot\boldsymbol{\sigma}/2\right) = \cos(\theta/2)\,I + i\,\boldsymbol{\sigma}\cdot n\,\sin(\theta/2)$.

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

$$D^{(\ell)}_{m0}(\varphi,\theta,0) = \sqrt{\frac{4\pi}{2\ell+1}}\,Y_\ell^{m*}(\theta,\varphi), \tag{142}$$

$$D^{(\ell)}_{m0}(0,\theta,\varphi) = (-)^m\sqrt{\frac{4\pi}{2\ell+1}}\,Y_\ell^{m*}(\theta,\varphi). \tag{143}$$

5 Combination of angular momenta

5.1 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

$$\boldsymbol{J} = \boldsymbol{j}_1 + \boldsymbol{j}_2. \tag{144}$$

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

$$|j_1, m_1\rangle \otimes |j_2, m_2\rangle, \tag{145}$$

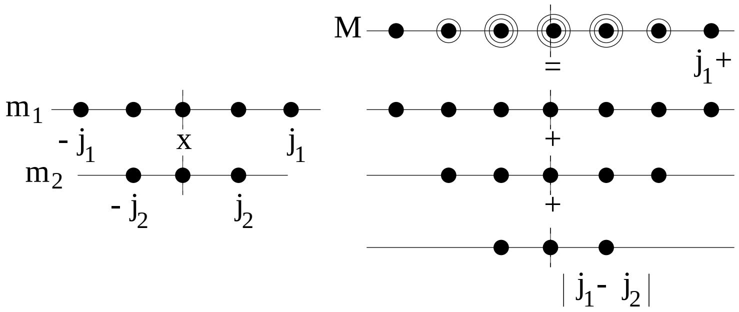
which we can write down since not only $[\boldsymbol{j}_1^2, j_{1z}] = [\boldsymbol{j}_2^2, j_{2z}] = 0$, but also $[j_{1m}, j_{2n}] = 0$. The sum-operator $\boldsymbol{J}$ obviously is not independent, but since the $\boldsymbol{J}$-operators again satisfy the well-known angular momentum commutation 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. 145, $[\boldsymbol{J}^2, j_{1z}] \neq 0$ and $[\boldsymbol{J}^2, j_{2z}] \neq 0$ (Note that $\boldsymbol{J}^2$ contains the operator combination $2\boldsymbol{j}_1 \cdot j_2$, which contains operators like j_{1x}, which do not commute with j_{1z}). It is easy to verify that one does have

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

and thus we can relabel the $(2j_1+1)(2j_2+1)$ states in Eq. 145 into states characterized with the quantum numbers

$$|j_1, j_2; J, M\rangle. \tag{146}$$

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

$$J = j_1 + j_2,\ j_1 + j_2 - 1, \ldots, |j_1 - j_2|, \tag{147}$$

going down in steps of one.

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

$$\sum_{J=|j_1-j_2|}^{j_1+j_2} (2J+1) = (2j_1+1)(2j_2+1). \tag{148}$$

Furthermore we have in combining angular momenta:

half-integer with half-integer ⟶ integer
integer with half-integer ⟶ half-integer
integer with integer ⟶ integer

5.2 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. 145,

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

1. The highest state has $M = 1$ and must be the first of the four states above. Thus for the labeling $|s_1, s_2; S, M\rangle$
$$|1/2, 1/2; 1, +1\rangle = |\uparrow\uparrow\rangle. \tag{149}$$
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

$$|1/2, 1/2; 1, 0\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \Big). \tag{150}$$

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

$$|1/2, 1/2; 1, -1\rangle = |\downarrow\downarrow\rangle. \tag{151}$$

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. 150. 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

   $$|1/2, 1/2; 0, 0\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \Big). \tag{152}$$

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

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

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

For the above case we have

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

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

$$|j_1, j_2; J, M\rangle = \sum_{m_1, m_2} C(j_1, m_1, j_2, m_2; J, M)\, |j_1, m_1\rangle \otimes |j_2, m_2\rangle. \tag{153}$$

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

$$|j_1, m_2\rangle \otimes |j_2, m_2\rangle = \sum_{J,M} C(j_1, m_1, j_2, m_2; J, M)\, |j_1, j_2; J, M\rangle. \tag{154}$$

In some cases (like combining two spin 1/2 states) one can make use of symmetry arguments. If a particular state has a well-defined symmetry under permutation of states 1 and 2, then all M-states belonging to a particular J-value have the same symmetry (because $j_{1\pm} + j_{2\pm}$ does not alter the symmetry. This could have been used for the 1/2 × 1/2 case, as the highest total M is symmetric, all $S = 1$ states are symmetric. This is in this case sufficient to get the state in Eq. 150.

We will give two other examples. The first is

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

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

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

The second is

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

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

5.3 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

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

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

$$\langle J'M'|S|J,M\rangle \sim \delta_{JJ'}\,\delta_{MM'}. \tag{155}$$

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

$$[J_x, V_\pm] = \mp\hbar V_z, \qquad [J_y, V_\pm] = -i\hbar V_z, \qquad [J_z, V_\pm] = \pm\hbar V_\pm, \tag{156}$$

or using $J_\pm$,

$$[J_+, V_+] = [J_-, V_-] = 0, \qquad [J_\pm, V_\mp] = \pm 2\hbar\, V_z. \tag{157}$$

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

$$J^2\, \boldsymbol{V}|J,M\rangle = \hbar^2 J(J+1)\, \boldsymbol{V}|J,M\rangle, \tag{158}$$

$$J_z\, V_\pm|J,M\rangle = (M\pm 1)\,\hbar\, V_\pm|J,M\rangle, \tag{159}$$

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

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

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

$$V_1^{\pm 1} = \mp\frac{V_x \pm i\,V_y}{\sqrt{2}}, \qquad V_1^0 = V_z. \tag{160}$$

These are chosen such that

$$[J_z, O_\ell^m] = m\,\hbar\, O_\ell^m \quad \text{and} \quad [J_\pm, O_\ell^m] = \hbar\sqrt{\ell(\ell+1) - m(m\pm 1)}\, O_\ell^{m\pm 1}, \tag{161}$$

for which one in general can write

$$\langle J'M'|O_\ell^m|J,M\rangle = C(\ell,m;J,M;J',M')\,\frac{\langle J'||O_\ell||J\rangle}{\sqrt{2J'+1}}. \tag{162}$$

The quantity $|J'||O_\ell||J\rangle$ 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.

6 Identical particles

6.1 Permutation symmetry

The hamiltonian for Z electrons in an atom,

$$H(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_Z; \boldsymbol{p}_1, \ldots, \boldsymbol{p}_Z) = \sum_{i=1}^{Z} \left(-\frac{\hbar^2}{2m} \boldsymbol{\nabla}_i^2 - \frac{Ze^2}{4\pi\epsilon_0\, r_i} \right) + \sum_{i>j}^{Z} \frac{e^2}{4\pi\epsilon_0\, |\boldsymbol{r}_i - \boldsymbol{r}_j|} \tag{163}$$

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

$$H(1 \ldots i \ldots j \ldots Z) = H(1 \ldots j \ldots i \ldots Z). \tag{164}$$

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

$$\phi^{S/A} = \phi(12) \pm \phi(21), \tag{165}$$

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

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

$$\phi^S = \phi(123) + \phi(213) + \phi(231) + \phi(321) + \phi(312) + \phi(132), \tag{166}$$

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

$$\phi^A = \phi(123) - \phi(213) + \phi(231) - \phi(321) + \phi(312) - \phi(132), \tag{167}$$

(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*

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

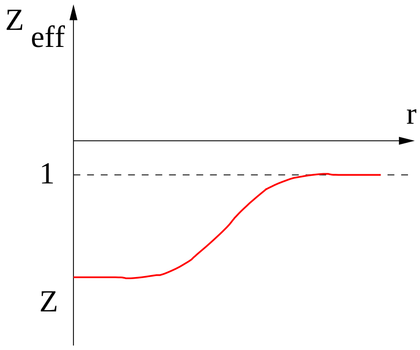
6.2 Applications

Bose-Einstein condensates

Bosons can reside in the same state. For instance by cooling down a gas of bosons they can all have momentum $\boldsymbol{p} = 0$. The wave function in momentum space would be a delta function, $\delta(\boldsymbol{p})$, leading to a single multi-boson system with macroscopic extension (in theory infinite for a true delta-function) in which all particles have lost their identity.

Atomic structure

The most well-known application of Fermi-Dirac statistics is the consecutive filling of atomic levels giving the periodic table of elements. For many-electron atoms a good starting point is trying to approximate the average effect of the electron-electron repulsion term in Eq. 163 into an effective central potential. The effective charge felt by an electron is expected to behave like

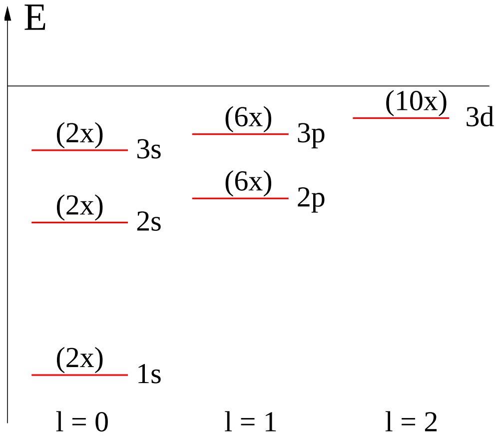


$$Z_{\text{eff}} \left\{ \begin{array}{l} \xrightarrow{r\to\infty} 1 \\ \xrightarrow{r\to 0} Z \end{array} \right.$$

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

$$H(\boldsymbol{r}_1,\dots,\boldsymbol{r}_Z;\boldsymbol{p}_1,\dots,\boldsymbol{p}_Z) \approx \sum_{i=1}^{Z}\left(-\frac{\hbar^2}{2m}\,\boldsymbol{\nabla}_i^2 - \frac{Z_{\rm eff}(r)\,e^2}{4\pi\epsilon_0\,r_i}\right) + \dots \tag{168}$$

The advantage of this procedure is that part of the repulsion is taken into account retaining a central interaction and a separable hamiltonian. This will modify the spectrum, lifting the degeneracy between different ℓ-values for given n. In general the higher ℓ values will because of the angular momentum contribution $\hbar^2\,\ell(\ell+1)/2m\,r^2$ in the effective radial potential will feel a smaller charge and hence become less bound.



The (schematic) spectrum for many-electron atoms. A possible parametrization of the levels taking into account the screening effect is

$$E_{n\ell} = -\frac{R_\infty}{(n-\delta_\ell)^2},$$

where δ_ℓ is referred to as quantum defect, and one expects $\delta_\ell \to 0$ for large ℓ-values. This will work particularly well for atoms with one electron outside a closed shell.

In the central field approximation, the hamiltonian is separable for the different electrons and the solution is an antisymmetrized product of single electron states (Slater determinant), where one needs to keep in mind the spin degeneracy (2 for each level). Operators compatible with the hamiltonian are $\boldsymbol{\ell}_i$ (and similarly spin operators), just as is the parity operator. Hence one has many good quantum numbers. At this level of approximation one can label the states by giving the various $(n\ell)$ levels and their multiplicities, e.g. for the ground state of helium $(1s)^2$, for Carbon $(1s)^2(2s)^2(2p)^2$, etc. Combining the angular momenta and spins into specific multiplets will be discussed as an application of spin but is not yet relevant, since all states are at this stage degenerate. This remains true if one refines the picture by using an effective central charge $Z_{\rm eff}(r)$. 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. $E_{\rm ionization}$ = 24.6 eV (He), 21.6 eV (Ne) and 15.8 eV (Ar). The level scheme in the table can also be used to establish the excited states.

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

7 Spin in Atomic Physics

7.1 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,

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

    for the spatial part.
  - The combination of the spins gives again an antisymmetric $S = 0$ and a symmetric $S = 1$ wave function.
  - The allowed configurations are thus obtained by the appropriate antisymmetric combinations of orbital and spin parts,

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

- 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

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

Summarizing in tabular form

Configurations in Helium							
configuration	$E^{(0)}/R_\infty$	L	S	Parity	Symmetry	J-configurations	# states
$(1s)^2$	-8	0	0	$+$	A	$^1S_{0+}$	1
			1	$+$	S	not allowed	3
$(1s)(2p)$ & $(2p)(1s)$	-5	1	0	$-$	S/A	$^1P_{1-}$	3
			1	$-$	S/A	$^3P_{0-,1-,2-}$	9
$(1s)(2s)$ & $(2s)(1s)$	-5	0	0	$+$	S/A	$^1S_{0+}$	1
			1	$+$	S/A	$^3S_{1+}$	3

Important to note is that although additional terms may be present in the full hamiltonian, the solutions found in this way do form a complete set of states for the atom. Other interaction terms give rise to shifts in the zeroth order energies and they may mix the states. To calculate such shifts we need to use perturbation theory.

7.2 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 $^2P \rightarrow ^2S$ is the well-known yellow Na-line in the visible spectrum, which by the fine-structure (see below) is split into two lines corresponding to the transitions $^2P_{3/2} \rightarrow ^2S_{1/2}$ and $^2P_{1/2} \rightarrow ^2S_{1/2}$. For atoms with *two* electrons outside a closed shell (Be, Mg, Ca, Sr, Ba, Ra) the multiplet structure resembles that of helium.

For a particular number of electrons it is easy to look at the number of possibilities to construct particular M_L and M_S values. This is denoted in a Slater diagram

$M_S \downarrow \; M_L$	-2	-1	0	$+1$	$+2$
$+1$	0	1	1	1	0
0	1	2	3	2	1
-1	0	1	1	1	0

It is easy to disentangle this into

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

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

7.3 Selection rules

For emission and absorption of light (photons) the relevant operator is the electric dipole operator, which in essence is the position operator. The calculation of transition probabilities are given by the matrix elements between the appropriate states. Since the dipole operator does not involve spin operators, the spin wave function doesn't change in a dipole transition, giving rise to a spin selection rule: $m_{s\,1} = m_{s\,2}$, i.e.

$$\Delta s = \Delta m_s = 0. \tag{169}$$

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 $\ell = 1$,

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

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

$$\Delta m_\ell = \pm 1, \tag{170}$$

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. 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

$$\Delta\ell = \pm 1. \tag{171}$$

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

$$\Delta J = 0,\ \pm 1 \tag{172}$$

(with $J = 0 \rightarrow J = 0$ forbidden!).

The interactions (absorption or emission) of photons in atoms can also proceed via different operators. The one treated here is known as electric dipole radiation (E1). In order of strength one has also the magnetic dipole radiation (M1), electric quadrupole radiation (E2), etc. For instance electric quadrupole radiation is governed by operators of the type $x_i\, x_j$, i.e. in a spherical representation the $\ell = 2$ spherical harmonics. This leads to transition selection rules in which parity is not changed and since the operators are proportional to $r^2\, Y_2^{m_\gamma}$ one has $\Delta\ell = 2$.

8 Bound state perturbation theory

8.1 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

$$E_n = E_n^{(0)} + \lambda\,E_n^{(1)} + \lambda^2\,E_n^{(2)} + \ldots, \tag{173}$$

$$|\psi_n\rangle = |\phi_n\rangle + \lambda\,|\psi_n^{(1)}\rangle, \tag{174}$$

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

$$\big(H_0 + \lambda\,V\big)\big(|\phi_n\rangle + \lambda\,|\psi_n^{(1)}\rangle + \ldots\big) = \big(E_n^{(0)} + \lambda\,E_n^{(1)} + \ldots\big)\big(|\phi_n\rangle + \lambda\,|\psi_n^{(1)}\rangle + \ldots\big). \tag{175}$$

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

$$\lambda\,V|\phi_n\rangle + \lambda\,H_0|\psi_n^{(1)}\rangle = \lambda\,E_n^{(1)}|\phi_n\rangle + \lambda\,E_n^{(0)}|\psi_n^{(1)}\rangle. \tag{176}$$

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

$$\lambda\,E_n^{(1)} = \langle\phi_n|\lambda\,V|\phi_n\rangle, \tag{177}$$

$$\lambda\big(E_n^{(0)} - E_m^{(0)}\big)\langle\phi_m|\psi_n^{(1)}\rangle = \langle\phi_m|\lambda\,V|\phi_n\rangle \quad (\text{for } m \neq n). \tag{178}$$

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,

$$E_n^{(1)} = \langle\phi_n|V|\phi_n = V_{nn}, \tag{179}$$

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n} |\phi_m\rangle\,\frac{\langle\phi_m|V|\phi_n\rangle}{E_n^{(0)} - E_m^{(0)}} = \sum_{m\neq n} |\phi_m\rangle\,\frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}}. \tag{180}$$

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. 175, giving

$$H_0|\psi_n^{(2)}\rangle + V|\psi_n^{(1)}\rangle = E_n^{(0)}|\psi_n^{(2)}\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle + E_n^{(2)}|\phi_n\rangle. \tag{181}$$

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

$$E_n^{(2)} = \langle\phi_n|V|\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{V_{nm}\,V_{mn}}{E_n^{(0)} - E_m^{(0)}}. \tag{182}$$

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

$$\sum_{m\neq n} \Rightarrow \sum_{m\neq n} + \int_0^\infty dE\,\rho(E), \tag{183}$$

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

8.2 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. 178 to 180 cannot be made. Eq. 178, however, also tells us how to proceed. Make sure that the states $|\phi_{n1}\rangle$, ..., $|\phi_{ns}\rangle$ which are degenerate with respect to H_0 are choosen to be eigenstates of the perturbation λV. In that case we can choose the wave function corrections orthogonal to all $|\phi_{nr}\rangle$ and we have $\langle\phi_{ni}|\lambda V|\phi_{nj}\rangle = 0$. The result is that we get instead of Eq. 180 the result

$$|\psi_n^{(1)}\rangle = \sum_{E_m^{(0)}\neq E_n^{(0)}} |\phi_m\rangle \, \frac{\langle\phi_m|V|\phi_n\rangle}{E_n^{(0)} - E_m^{(0)}}. \tag{184}$$

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.

8.3 Applications

Fine structure in hydrogen: the mass correction

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

$$H = H_0 + H_{\rm mass} + H_{\rm Foldy} + H_{\rm so} \tag{185}$$

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

$$H_{\rm mass} = \sqrt{\boldsymbol{p}^2c^2 + m^2c^4} - mc^2 - \frac{\boldsymbol{p}^2}{2m} \approx -\frac{\boldsymbol{p}^4}{8m^3c^2}. \tag{186}$$

Including this correction, the operators $\boldsymbol{\ell}^2$ and ℓ_z still remain compatible with the hamiltonian, but the radial dependence now will be modified. However in *first order perturbation theory* one obtains an accurate estimate of the energy shifts by calculating the expectation value of the correction. We here just state the result (treated in many quantum mechanics books),

$$\Delta E_{\rm mass}(n\ell) = \langle n\ell m\ldots| - \frac{\boldsymbol{p}^4}{8m^3c^2}|n\ell m\ldots\rangle = -\alpha^2\,\frac{R_\infty}{n^3}\left(\frac{1}{\ell+\frac{1}{2}} - \frac{3}{4n}\right). \tag{187}$$

Fine structure in hydrogen: the spin-orbit interaction

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

$$H_{\rm so} = \frac{1}{2m^2c^2}\,\frac{1}{r}\,\frac{dV_c}{dr}\,\boldsymbol{\ell}\cdot\boldsymbol{s}. \tag{188}$$

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 $\langle n\ell s m_\ell' m_s'|H_{\rm so}|n\ell s m_\ell m_s\rangle$, there is a smarter way. By rewriting

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

one sees that the operators $\boldsymbol{\ell}^2$, $\boldsymbol{s}^2$, $\boldsymbol{j}^2$ and j_z (which from the theory of addition of angular momenta are known to be compatible with each other) are also compatible with the hamiltonian. This is not true for the set $\boldsymbol{\ell}^2$, $\boldsymbol{s}^2$, ℓ_z and s_z. Hence if we use states $|n\ell s j m\rangle$, the correction term has no off-diagonal elements, hence does (for given ℓ and s not mix the unperturbed degenerate states and the splitting for the correct combinations of states is directly found as

$$\begin{aligned}
\Delta E_{\rm so}(n\ell s j m) &= \frac{1}{2m^2c^2}\langle n\ell s j m|\frac{1}{r}\,\frac{dV_c}{dr}\,\boldsymbol{\ell}\cdot\boldsymbol{s}|n\ell s j m\rangle \\
&= \frac{e^2\,\hbar^2}{32\pi\epsilon_0\,m^2c^2}\,\langle n\ell|\frac{1}{r^3}|n\ell\rangle\;[j(j+1)-\ell(\ell+1)-s(s+1)] \\
&= \frac{e^2\,\hbar^2}{32\pi\epsilon_0\,m^2c^2}\,\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{a_0^3\,n^3\,\ell(\ell+1)(\ell+\frac{1}{2})} \qquad (189)
\end{aligned}$$

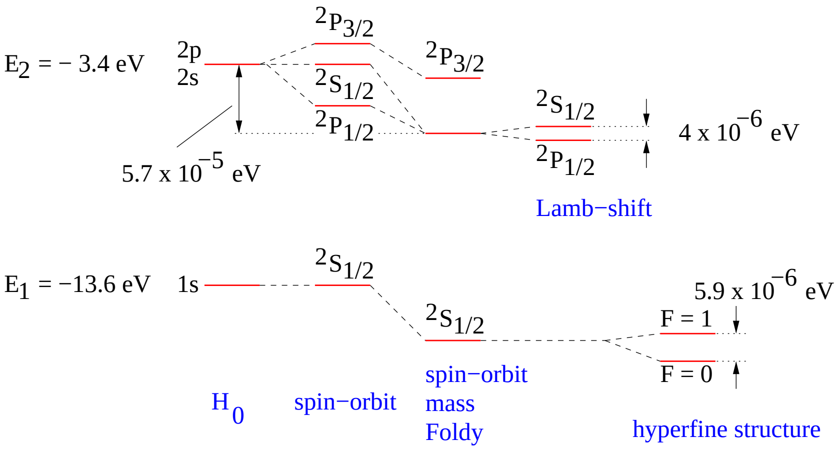
We thus must couple ℓ and s to j-eigenstates. For one electron with a given $\ell \neq 0$ there are two possibilities for j, namely $j = \ell \pm \frac{1}{2}$ giving for $\ell \neq 0$

$$\Delta E_{\rm so}(n\ell j) = \alpha^2\,\frac{R_\infty}{n^3}\left(\frac{1}{\ell+\frac{1}{2}} - \frac{1}{j+\frac{1}{2}}\right) \qquad (190)$$

and for the combined result

$$\Delta E_{\rm mass\,+\,so} = -\alpha^2\,\frac{R_\infty}{n^3}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right) \qquad (191)$$

In the Hydrogen atom one also has the Foldy term, which is a relativistic correction proportional to $\delta^3(\boldsymbol{r})$ and thus only affects s-waves. It makes the above equation valid also for s-waves. Schematically (not on scale) one has the following fine structure in the hydrogen spectrum



The various terms cause shifts in the order of 10^{-4} eV, giving within a orbit characterized by the principal quantum number n states with well-defined j-values. We denote such a level with a *term symbol*, for hydrogen

$$(n\ell)\,^{(2S+1)}L_J$$

where $(n\ell)$ indicates the spatial part of the electron wave function, $2S+1$ is the total spin multiplicity and L is the total orbital angular momentum of the electrons (using notation $S, P, D, \ldots$ for $L = 0, 1, 2, \ldots$). In this specific case of hydrogen with just one electron $S = 1/2$ and the multiplicity is always 2 while $L = \ell$. The splitting of the $^2S_{1/2}$ and $^2P_{1/2}$ is about 4×10^{-6} eV produces a splitting of the Lyman α line. Also transitions between both levels are possible via an E1 transition with frequency of about 1 GHz.

Fine structure in hydrogen: the hyperfine splitting

The hyperfine structure in hydrogen is due to the interaction of the magnetic moments of electron and nucleus. Also the proton has a magnetic moment, which induces a magnetic dipole field felt by the electron and vice versa. It produces an interaction term, which for s-waves is of the form

$$V_{ss} = \frac{1}{6\pi\epsilon_0\, c^2}\, \boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_p\, \boldsymbol{\nabla}^2\, \frac{1}{r}. \tag{192}$$

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

$$\Delta E_{ss} \propto g_e\, g_p\, \langle|\boldsymbol{S}\cdot\boldsymbol{I}|\rangle = \frac{1}{2}\, g_e\, g_p\, \hbar^2\, \left[F(+F1) - S(S+1) - I(I+1)\right]. \tag{193}$$

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.

The fine structure of atoms

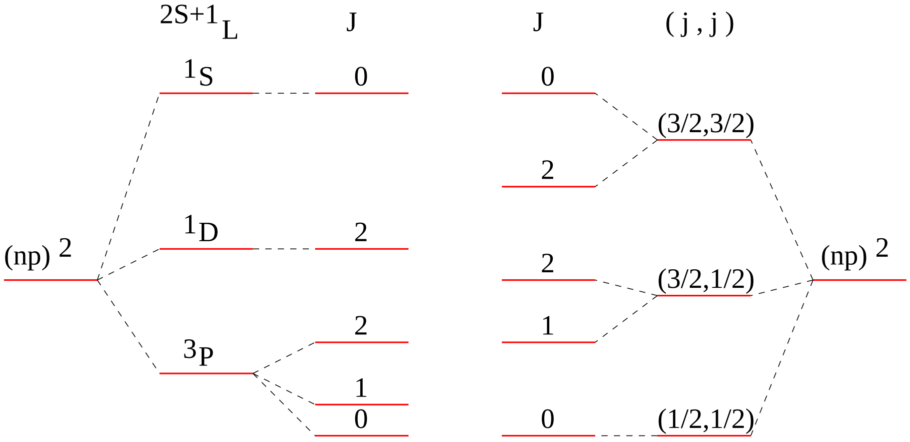
When combining angular momenta, we discussed the multiplets forming the fine structure in atoms. For not too heavy atoms, the splitting of energies within the multiplets turn out to be described well by a spin-orbit interaction of the form

$$H_{\rm so} = A(L,S)\,\boldsymbol{L}\cdot\boldsymbol{S}, \tag{194}$$

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

$$\Delta E(LSJM) = \frac{1}{2}\, A\hbar^2\left[J(J+1) - L(L+1) - S(S+1)\right]. \tag{195}$$

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

$$r = \frac{E(^{2S+1}L_J) - E(^{2S+1}L_{J-1})}{E(^{2S+1}L_{J-1}) - E(^{2S+1}L_{J-2})} = \frac{J}{J-1}, \tag{196}$$

e.g. for the ratio $(E(^3P_2) - E(^3P_1))/(E(^3P_1) - E(^3P_0))$ one expects $r = 2$ if LS-coupling describes the fine structure. For Carbon the actual ratio is 1.65, for Silicium (Si) it is 1.89, but for a heavy atom as lead (Pb) the result is just 0.36, indicating a different type of fine structure. A different scheme is the jj-scheme in which first the orbital angular momenta and spins of the electrons are coupled, which in turn are combined into J-values, illustrated in the figure for the $(np)^2$ configuration. Note that coupling two identical j-values of the electrons, one needs to account for the symmetry of the wave function. The wave function for the maximal $J = 2\,j$ is symmetric, for the next lower J it is antisymmetric, then again symmetric, etc. This explains the J-values in the jj-coupling scheme. In the final result the same J-values must appear, but note that the actual wave functions are different.

9 Magnetic effects in atoms and the electron spin

9.1 The Zeeman effect

Interaction of orbital angular momentum with magnetic field

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

$$H = \underbrace{-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \frac{Ze^2}{4\pi\epsilon_0\, r}}_{H_0} + V_{\rm mag}, \tag{197}$$

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

$$\boldsymbol{\mu}_\ell = -g_\ell\,\frac{e}{2m}\,\boldsymbol{\ell} \tag{198}$$

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

$$\Delta E_{n\ell m_\ell} = \langle n\ell m_\ell|\frac{eB}{2m}\,\ell_z|n\ell m_\ell\rangle = m_\ell\,\mu_B B, \tag{199}$$

where

$$\mu_B = \frac{e\hbar}{2m} = \frac{1}{2}\,e\,c\,\frac{\hbar}{mc} \approx 5.8\times 10^{-5}\ \text{eV/T} \tag{200}$$

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.

$$V_{\rm mag} = -\boldsymbol{\mu}_s\cdot\boldsymbol{B}, \tag{201}$$

with

$$\boldsymbol{\mu}_s = -g_s\,\frac{e}{2m}\,\boldsymbol{s} = -g_s\,\frac{e\hbar}{m}\,\boldsymbol{\sigma}. \tag{202}$$

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

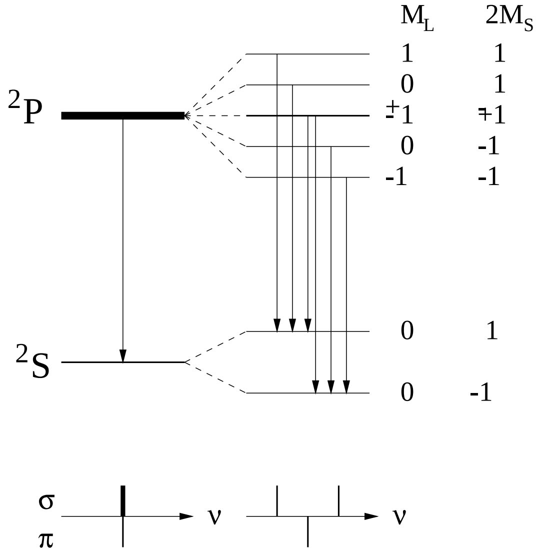
In general a ${}^{2S+1}L$ level in a magnetic field is split by an interaction term

$$V_{\rm mag} = -\boldsymbol{\mu}\cdot\boldsymbol{B}, \tag{203}$$

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

$$\Delta E(LSM_LM_S) = -\mu_B B(M_L + 2\,M_S). \tag{204}$$

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.

9.2 Spin-orbit interaction and magnetic fields

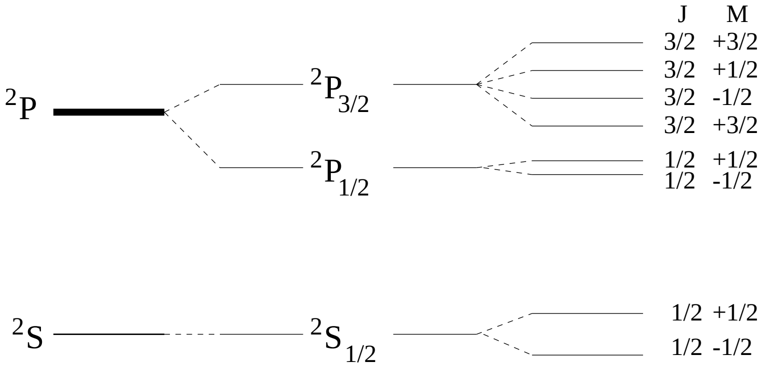
Inclusion of the spin-orbit interaction is important to describe the fine structure of the multiplets in atomic spectra. This fine structure in general turns out to be considerably larger than the magnetically induced splittings. In that case one cannot simply use the results for the normal Zeeman effect when spin plays a role. So consider the situation that one has an interaction term in the atom of the form

$$H_{\rm int} = A\,\boldsymbol{L}\cdot\boldsymbol{S} - \boldsymbol{\mu}\cdot\boldsymbol{B}, \tag{205}$$

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

$$\begin{aligned} A = 0: &\quad \text{eigenstates} \quad |(\ldots)LSM_LM_S\rangle, \\ &\quad \Delta E(LSM_LM_S) = \mu_B B(M_L + 2M_S), \\[2em] B = 0: &\quad \text{eigenstates} \quad |(\ldots)LSJM\rangle, \\ &\quad \Delta E(LSJM) = \frac{1}{2}\,A\hbar^2\left[J(J+1) - L(L+1) - S(S+1)\right]. \end{aligned}$$

The splitting pattern for $A = 0$ has already been given, for $B = 0$ it splits the ${}^{2S+1}L$ multiplet into the different ${}^{2S+1}L_J$ multiplets, for the ${}^2P \rightarrow {}^2S$ transition indicated as the first splitting in the figure below.



The spin-orbit splitting leading to the ${}^{2S+1}L_J$ multiplets for the ${}^2P$ and ${}^2S$ levels and the consecutive splitting in a magnetic field for the case of a small magnetic field.

When one switches on the magnetic field, one deals with an interaction term for which neither $|LSM_LM_S\rangle$, nor $|LSJM\rangle$ are proper states (check compatibility of the relevant operators!). If the magnetic field is small the states will be in first order given by $|LSJM\rangle$ and one can calculate the energy shift via

$$\Delta E_{\rm mag} = \mu_B B\,\langle(\ldots)LSJM|L_z + 2S_z|(\ldots)LSJM\rangle = \mu_B B\,\langle(\ldots)LSJM|J_z + S_z|(\ldots)LSJM\rangle. \tag{206}$$

The part with which we need to be careful is the expectation value of S_z, Evaluating it between states with different M-values belonging to the same J gives zero, because if two M values involve the same M_S, the M_L's must be different (remember that in the coupling $M = M_L + M_S$). Thus we just need

$$\langle LSJM|S_z|LSJM\rangle = M\,\frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{207}$$

which follows from a subtle relation involving $\boldsymbol{S}$ and $\boldsymbol{J}$ operators[3], $\boldsymbol{J}^2 S_z + S_z \boldsymbol{J}^2 = 2\,J_z\,(\boldsymbol{J}\cdot\boldsymbol{S})$ leading to

$$\Delta E_{\rm mag} = \underbrace{\left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}\right]}_{g_J} M\,\mu_B B, \tag{208}$$

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.

---

[3] 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.

10 Variational approach

10.1 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,

$$E_{[\alpha_1,\alpha_2,\ldots]} = \frac{\langle\psi_{[\alpha_1,\alpha_2,\ldots]}|H|\psi_{[\alpha_1,\alpha_2,\ldots]}\rangle}{\langle\psi_{[\alpha_1,\alpha_2,\ldots]}|\psi_{[\alpha_1,\alpha_2,\ldots]}\rangle}. \tag{209}$$

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

$$E_{[\alpha_1,\alpha_2,\ldots]} \geq E_0, \tag{210}$$

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,

$$\frac{\partial E_{[\alpha_1,\alpha_2,\ldots]}}{\partial\alpha_i} = 0, \tag{211}$$

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.

10.2 Application: ground state of Helium atom

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

$$\psi_T(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{\alpha^3}{\pi\, a_0^3}\, e^{-\alpha\, r_1/a_0}\, e^{-\alpha\, r_2/a_0}. \tag{212}$$

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

$$\langle\psi_T| - \frac{\hbar^2}{2m}\left(\boldsymbol{\nabla}_1^2 + \boldsymbol{\nabla}_2^2\right)|\psi_T\rangle = \frac{\hbar^2}{m\, a_0^2}\,\alpha^2 = 2\,\alpha^2\, R_\infty, \tag{213}$$

$$\langle\psi_T|\frac{-Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)|\psi_T\rangle = -\frac{2Ze^2}{4\pi\epsilon_0\, a_0}\,\alpha = -4\, Z\alpha\, R_\infty, \tag{214}$$

$$\langle\psi_T|\frac{e^2}{4\pi\epsilon_0\, r_{12}}|\psi_T\rangle = \frac{5}{4}\,\alpha\, R_\infty, \tag{215}$$

and thus

$$E_{[\alpha]} = 2\left[\alpha^2 - \left(2Z - \frac{5}{8}\right)\alpha\right] R_\infty, \tag{216}$$

which is minimized for

$$\alpha = Z_{\text{eff}} = Z - \frac{5}{16} \tag{217}$$

with

$$E[\alpha_{\text{min}}] = -2\left(Z - \frac{5}{16}\right)^2 R_\infty. \tag{218}$$

For He this gives $E_{\text{gs}} = -5.7\, R_\infty$, wich is within a few percent of the experimental value of $-5.81\, R_\infty =$ 79.0 eV and much better than the perturbative value discussed in section 8.3 (which of course is just the result obtained for $\alpha = 2$). As expected the value $Z_{\text{eff}} = 27/16$ is less than 2.

10.3 Application: ionization energies and electron affinities

Some results that we have encountered in previous sections are

$$\begin{aligned} \text{H}^+ + e^- &= \text{H} + \ 13.6 \text{ eV}, \\ \text{He}^{++} + e^- &= \text{He}^+ + \ 54.4 \text{ eV}, \end{aligned}$$

Adding another electron in the latter case yields

$$\text{He}^+ + e^- = \text{He} + \ 24.6 \text{ eV}, \tag{219}$$

showing that adding electrons one gains less energy if there are already other electrons. The energy one gains in adding the last electron is the *ionization energy.* In many cases one can still add additional electrons and gain some energy, which is called the *electron affinity* E.g. for Chlorine

$$\begin{aligned} \text{Cl}^+ + e^- &= \text{Cl} + \ 13.0 \text{ eV}, \\ \text{Cl} + e^- &= \text{Cl}^- + \ 3.6 \text{ eV}. \end{aligned}$$

The binding energy of Chlorine is 13.0 eV, the electron affinity is 3.6 eV. Electron affinities play a role in molecular binding.

An interesting example is actually the hydrogen atom, which also has a positive electron affinity,

$$\text{H} + e^- = \text{H}^- + \ 0.76 \text{ eV}.$$

The H atom, however, also illustrates that adding a second electron completely changes the structure of the wave functions. Adding one electron to H^+ or He^{++} one has simple hydrogen-like wave functions. But adding the second electron one has to account for the presence of the other electron as illustrated for He using the variational approach. In that case a product wave function still worked fine. If one tries for a second electron in H^- such a product wave function one does not find a positive electron affinity. In order to find a positive electron affinity for the H-atom (for which an equivalent statement is that the H^--ion has a binding energy of $0.056\, R_\infty = 0.76$ eV) one can use e.g. a trial function of the form

$$\psi_T = C\left[e^{-(\alpha_1 r_1 + \alpha_2 r_2)/a_0} + e^{-(\alpha_1 r_2 + \alpha_2 r_1)/a_0}\right]. \tag{220}$$

The form is suggestive for two different orbits with fall-off parameters α_1 and α_2, but as electrons are indistinguishable one must (anti)-symmetrize (depending on spin) the two terms. With a plus sign one has wave functions without nodes giving the lowest energy.

11 Time-dependent perturbation theory

11.1 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

$$\psi(t) = \sum_n c_n(t)\phi_n, \tag{221}$$

insert this in the Schrödinger equation,

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi(t) \tag{222}$$

leading to

$$i\hbar\dot{c}_n(t) = E_n\,c_n(t) \quad\Longrightarrow\quad c_n(t) = c_n\,e^{-i\,E_n t/\hbar}, \tag{223}$$

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
$$\psi(t) = \phi_i\,e^{-iE_i t/\hbar}, \tag{224}$$
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
$$\psi(t) = c_1\,\phi_1\,e^{-iE_1 t/\hbar} + c_2\,\phi_2\,e^{-iE_2 t/\hbar}, \tag{225}$$
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.

$$H = H_0 + V(t). \tag{226}$$

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

$$\psi(t) = \sum_n c_n(t)\,\phi_n\,e^{-iE_n t/\hbar}. \tag{227}$$

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,

$$i\hbar\frac{\partial}{\partial t}\psi(t) = (H_0 + V(t))\,\psi(t), \tag{228}$$

one simply finds

$$i\hbar\,\dot{c}_p(t) = \sum_n V_{pn}(t)\,c_n(t)\,e^{+i\,\omega_{pn}t}, \tag{229}$$

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.

11.2 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

$$\phi_a \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \phi_b = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{230}$$

the Hamiltonian H_0 and the perturbation V are taken to be

$$H_0 = \begin{pmatrix} E_a & 0 \\ 0 & E_b \end{pmatrix} \quad \text{and} \quad V = \begin{pmatrix} V_{aa}(t) & V_{ab}(t) \\ V_{ba}(t) & V_{bb}(t) \end{pmatrix} = \begin{pmatrix} 0 & V_{ab}(t) \\ V_{ab}^*(t) & 0 \end{pmatrix}. \tag{231}$$

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

$$\psi(t) = c_a(t) \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-iE_at/\hbar} + c_b(t) \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{-iE_bt/\hbar} = \begin{pmatrix} c_a(t)\,e^{-iE_at/\hbar} \\ c_b(t)\,e^{-iE_bt/\hbar} \end{pmatrix}, \tag{232}$$

and the coefficients $c_a(t)$ and $c_b(t)$ obey a simple coupled set of equations of the form

$$\begin{aligned} i\hbar \begin{pmatrix} \dot{c}_a(t) \\ \dot{c}_b(t) \end{pmatrix} &= \begin{pmatrix} 0 & V_{ab}(t)\,e^{+i\omega_{ab}t} \\ V_{ab}^*(t)\,e^{-i\omega_{ab}t} & 0 \end{pmatrix} \begin{pmatrix} c_a(t) \\ c_b(t) \end{pmatrix} \\ &\equiv \hbar \begin{pmatrix} 0 & v(t) \\ v^*(t) & 0 \end{pmatrix} \begin{pmatrix} c_a(t) \\ c_b(t) \end{pmatrix}, \end{aligned} \tag{233}$$

representing simple coupled equations,

$$i\,\dot{c}_a(t) = v(t)\,c_b(t), \tag{234}$$

$$i\,\dot{c}_b(t) = v^*(t)\,c_a(t), \tag{235}$$

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,

$$H = -\boldsymbol{\mu}\cdot\boldsymbol{B}(t) = -\gamma\,\boldsymbol{s}\cdot\boldsymbol{B}(t), \tag{236}$$

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

$$H_0 = -\frac{\gamma B_0}{2}\,\hbar\,\sigma_z = -\frac{\gamma B_0}{2}\,\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{237}$$

The solutions are easily obtained,

$$\phi_a = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{with} \quad E_a = -\frac{\gamma B_0}{2}\,\hbar, \tag{238}$$

$$\phi_b = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{with} \quad E_b = \frac{\gamma B_0}{2}\,\hbar, \tag{239}$$

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

$$\begin{aligned} H &= -\frac{\gamma B_0}{2}\,\hbar\,\sigma_z - \frac{\gamma B_1}{2}\,\hbar(\sigma_x\,\cos\omega t + \sigma_y\,\sin\omega t) \\ &= -\frac{\gamma B_0}{2}\,\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \frac{\gamma B_1}{2}\,\hbar \begin{pmatrix} 0 & e^{-i\omega t} \\ e^{+i\omega t} & 0 \end{pmatrix}. \end{aligned} \tag{240}$$

We thus have a harmonic perturbation of the form

$$V_{ab}(t) = -\frac{\gamma B_1}{2}\,e^{-i\omega t} \quad \text{and} \quad v(t) = \frac{V_{ab}(t)}{\hbar}\,e^{+i\omega_{ab}t} = v_1\,e^{-i(\omega-\omega_{ab})t}. \tag{241}$$

with $v_1 = -\gamma B_1/2$.

The coupled equations in Eq. 233 can now simply be rewritten into a second order differential equation for c_a,

$$\ddot{c}_a + i(\omega - \omega_{ab})\,\dot{c}_a + v_1^2\,c_a = 0. \tag{242}$$

This equation has two independent solutions of the form $e^{i\,pt}$ with

$$p = -\frac{1}{2}\,(\omega - \omega_{ab}) \pm \omega_r \tag{243}$$

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

$$\begin{aligned} c_a(t) &= e^{-\frac{1}{2}i(\omega-\omega_{ab})t}\left(A\,\sin(\omega_r\,t) + B\,\cos(\omega_r\,t)\right), \\ c_b(t) &= \frac{i}{v(t)}\,\dot{c}_a(t). \end{aligned} \tag{244}$$

Starting off with $c_a(0) = 0$ and $|c_b(0)| = 1$, it is straightforward to check that

$$c_a(t) = A\,e^{-\frac{1}{2}\,i\,(\omega-\omega_{ab})t}\,\sin(\omega_r\,t), \tag{245}$$

$$|A|^2 = \frac{v_1^2}{\omega_r^2} = \frac{\gamma^2 B_1^2}{(\omega - \omega_{ab})^2 + \gamma^2 B_1^2}, \tag{246}$$

$$|c_a(t)|^2 + |c_b(t)|^2 = 1. \tag{247}$$

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 $\omega_r = |v_1|$).

11.3 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

$$c_p(t) = c_p^{(0)}(t) + \lambda\, c_p^{(1)}(t) + \ldots, \tag{248}$$

the time-dependence of a specific order is determined by the next lower order,

$$i\hbar\, \dot{c}_p^{(m+1)} = \sum_n V_{pn}(t)\, c_n^{(m)}(t)\, e^{+i\,\omega_{pn} t}. \tag{249}$$

Starting with $c_p(0) = \delta_{pi}$, one immediately sees that the first two orders are given by

$$c_p^{(0)}(\tau) = \delta_{pi}, \tag{250}$$

$$c_p^{(1)}(\tau) = \frac{1}{i\hbar}\int_0^\tau dt\; V_{pi}(t)\, e^{+i\,\omega_{pi} t}. \tag{251}$$

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 $i \rightarrow p$. 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,

$$\begin{aligned} c_p^{(1)}(\tau) &= \frac{|V_{pi}|}{i\hbar}\int_0^\tau dt\; e^{-i(\omega-\omega_{pi})t} = \frac{|V_{pi}|}{\hbar(\omega-\omega_{pi})}\, e^{-i(\omega-\omega_{pi})t}\Big|_0^\tau \\ &= \frac{|V_{pi}|}{\hbar(\omega-\omega_{pi})}\left(1 - e^{-i(\omega-\omega_{pi})\tau}\right) = \frac{2\,|V_{pi}|}{\hbar(\omega-\omega_{pi})}\,\sin((\omega-\omega_{pi})\tau/2)\, e^{-i\,(\omega-\omega_{pi})\tau/2}, \end{aligned} \tag{252}$$

and thus for $p \neq i$,

$$P_{i\rightarrow p}^{(1)}(\tau) = \frac{4\,|V_{pi}|^2}{\hbar^2}\,\frac{\sin^2((\omega-\omega_{pi})\tau/2)}{(\omega-\omega_{pi})^2}. \tag{253}$$

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

$$\int d\omega\; \frac{\sin^2(\omega\tau/2)}{\omega^2} = \frac{\pi\,\tau}{2}, \tag{254}$$

we approximate

$$\frac{\sin^2(\omega\tau/2)}{\omega^2} = \frac{\pi\,\tau}{2}\,\delta(\omega). \tag{255}$$

Then we find[4]

$$P_{i\rightarrow p}^{(1)}(\tau) = \tau\,\frac{2\pi}{\hbar}\,|V_{pi}|^2\,\delta(E_p - E_i - Q) \tag{256}$$

---

[4] $\delta(ax) = \frac{1}{|a|}\,\delta(x)$

where $Q = \hbar\omega$, or for the transition probability per unit time,

$$W_{i\rightarrow p} \approx \dot{P}^{(1)}_{i\rightarrow p} = \frac{2\pi}{\hbar}\,|V_{pi}|^2\,\delta(E_p - E_i - Q) \qquad \text{Fermi's Golden Rule.} \tag{257}$$

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

$$W_{i\rightarrow f} \approx \int dE_p\,\rho_f(E_p)\,\frac{2\pi}{\hbar}\,|V_{fi}|^2\,\delta(E_p - E_i - Q) = \frac{2\pi}{\hbar}\,|V_{fi}|^2\,\rho_f(E_i + Q) \tag{258}$$

(Fermi's Golden Rule No. 2).

12 Emission and absorption of radiation and lifetimes

12.1 Application: emission and absorption of radiation by atoms

We take a plane wave for the scalar and vector potential,

$$\phi = \tilde{\phi}(\boldsymbol{k},\omega)\ \exp[i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)], \tag{259}$$

$$\boldsymbol{A} = \tilde{\boldsymbol{A}}(\boldsymbol{k},\omega)\ \exp[i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)], \tag{260}$$

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[5]

$$\boldsymbol{E} = \tilde{\boldsymbol{E}}(\boldsymbol{k},\omega)\ \exp[i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)], \tag{261}$$

$$\boldsymbol{B} = \tilde{\boldsymbol{B}}(\boldsymbol{k},\omega)\ \exp[i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)]. \tag{262}$$

The interaction of matter with an electromagnetic field is given by

$$H_{int} = \int d^3r\ \left[\rho(\boldsymbol{r})\,\phi(\boldsymbol{r}) - \boldsymbol{j}(\boldsymbol{r})\cdot\boldsymbol{A}(\boldsymbol{r})\right], \tag{263}$$

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

$$\exp[i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)] = e^{-i\,\omega t}\,(1 + i\,\boldsymbol{k}\cdot\boldsymbol{r} + \ldots). \tag{264}$$

One obtains

$$\begin{aligned} H_{int} &= e^{-i\omega t}\int d^3r\ \Big[(1+i\,\boldsymbol{k}\cdot\boldsymbol{r})\,\rho(\boldsymbol{r})\,\tilde{\phi}(\boldsymbol{k},\omega) - (1+i\,\boldsymbol{k}\cdot\boldsymbol{r})\,\boldsymbol{j}(\boldsymbol{r})\cdot\tilde{\boldsymbol{A}}(\boldsymbol{k},\omega)\Big] && (265)\\ &= e^{-i\omega t}\Big[Q\,\tilde{\phi}(\boldsymbol{k},\omega) - \boldsymbol{D}\cdot\tilde{\boldsymbol{E}}(\boldsymbol{k},\omega) - \boldsymbol{\mu}\cdot\tilde{\boldsymbol{B}}(\boldsymbol{k},\omega) + \ldots\Big], && (266)\end{aligned}$$

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,

$$Q = \int d^3r\ \rho(\boldsymbol{r}) \Longrightarrow \sum_i q_i, \tag{267}$$

$$\boldsymbol{D} = \int d^3r\ \boldsymbol{r}\,\rho(\boldsymbol{r}) \Longrightarrow \sum_i q_i\,\boldsymbol{r}_i, \tag{268}$$

$$\boldsymbol{\mu} = \int d^3r\ \boldsymbol{r}\times\boldsymbol{j}(\boldsymbol{r}) \Longrightarrow \sum_i \frac{q_i}{m_i}\,\boldsymbol{\ell}_i, \tag{269}$$

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 ($\boldsymbol{D}$).

---

[5] 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

$$\boldsymbol{A} = \boldsymbol{\epsilon}(\boldsymbol{k},\omega)\,\frac{c\,\tilde{E}_0(\boldsymbol{k},\omega)}{i\,\omega}\,\exp[i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)] \tag{270}$$

and $\phi = 0$. The vector $\boldsymbol{\epsilon}$ is called the polarization. One has

$$\boldsymbol{E} = \boldsymbol{\epsilon}\,\tilde{E}_0\,\exp[i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)], \tag{271}$$

$$\boldsymbol{B} = \frac{\boldsymbol{k}\times\boldsymbol{\epsilon}}{|\boldsymbol{k}|}\,\tilde{E}_0\,\exp[i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)]. \tag{272}$$

In the dipole approximation the interaction with matter is given by

$$V(t) = -\boldsymbol{D}\cdot\boldsymbol{E}(t) = -\boldsymbol{D}\cdot\boldsymbol{\epsilon}\,\tilde{E}_0\,e^{-i\,\omega t}. \tag{273}$$

Although we have a time-dependent interaction, we can proceed as in the derivation of Fermi's golden rule. We obtain now

$$c_p^{(1)}(\tau) = \frac{\langle\phi_p|\boldsymbol{D}\cdot\boldsymbol{\epsilon}|\phi_i\rangle\,E_0}{i\hbar}\,\frac{e^{i\,(\omega_{pi}-\omega)\tau}-1}{i\,(\omega_{pi}-\omega)}, \tag{274}$$

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 $\omega \rightarrow -\omega$. 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

$$P^{(1)}_{i\rightarrow p}(\tau) = \frac{E_0^2(\omega)}{\hbar^2}\,|\langle\phi_p|\boldsymbol{D}\cdot\boldsymbol{\epsilon}|\phi_i\rangle|^2\,\frac{\pi\,\tau}{2}\,\delta(\omega-|\omega_{pi}|). \tag{275}$$

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 $d\omega$,

$$\frac{1}{2}\,\epsilon_0\,E_0^2(\omega)\,d\omega = \frac{N(\omega)\,\hbar\omega}{c}\,d\omega. \tag{276}$$

Integrating over the photon frequencies, one sees that the atom absorps or emits photons of the right frequency leading to a transition rate

$$\dot{P}^{(1)}_{i\rightarrow p} = \frac{\pi}{\epsilon_0\,\hbar c}\,|\omega_{pi}|\,N(|\omega_{pi}|)\,|\langle\phi_p|\boldsymbol{D}\cdot\boldsymbol{\epsilon}|\phi_i\rangle|^2. \tag{277}$$

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

$$W_{i\rightarrow p} = \overline{\dot{P}^{(1)}_{i\rightarrow p}} = \frac{4}{3}\,\pi^2\,\alpha\,|\omega_{pi}|\,N(|\omega_{pi}|)\,|\langle\phi_p|\boldsymbol{R}|\phi_i\rangle|^2. \tag{278}$$

Note that by treating also the electromagnetic field quantummechanically one finds in addition to the *stimulated absorption or emission* rate a *spontaneous emission* rate

$$W^{\text{spont.}}_{i\rightarrow p} = \frac{4}{3}\,\alpha\,\frac{\omega_{ip}^3}{c^2}\,|\langle\phi_p|\boldsymbol{R}|\phi_i\rangle|^2, \tag{279}$$

governed by the same transition matrix element and thus obeying the same selection rules.

12.2 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

$$P(t) = P(0)\,e^{-\gamma\,t} = P(0)\,e^{-t/T}, \tag{280}$$

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

$$|\psi_n(t)\rangle \propto e^{-i\,E_n t/\hbar - \gamma_n t/2}. \tag{281}$$

We can expand a decaying state in eigenmodes according to

$$e^{-i\,E_n t/\hbar-\gamma_n t/2}\,\theta(t) = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,c(\omega)\,e^{-i\,\omega t}, \tag{282}$$

(including the Heavyside step function θ) with

$$\begin{aligned}
c(\omega) &= \int_0^\infty dt\ e^{+i\,(\omega-\omega_n+i\gamma_n/2)t}\\
&= \left.\frac{-i}{\omega-\omega_n+i\gamma_n/2}e^{+i\,(\omega-\omega_n+i\gamma_n/2)t}\right|_0^\infty\\
&= \frac{i}{\omega-\omega_n+i\gamma_n/2}.
\end{aligned} \tag{283}$$

For unstable states the transition amplitude for emission or absorption of a photon is then proportional to

$$\begin{aligned}
T(\omega) &= \int\frac{d\omega_1'}{2\pi}\,\frac{d\omega_2'}{2\pi}\,c_2^*(\omega_2')\,c_1(\omega_1')\,2\pi\,\delta(\omega-\omega_1'+\omega_2')\\
&= \int\frac{d\omega'}{2\pi}c_2^*(\omega')\,c_1(\omega'+\omega)\\
&= \int\frac{d\omega'}{2\pi}\int_0^\infty dt_1\int_0^\infty dt_2\ e^{-i\,(\omega'-\omega_2-i\gamma_2/2)t_2}\ e^{+i\,(\omega'+\omega-\omega_1+i\gamma_1/2)t_1}\\
&= \int_0^\infty dt_1\int_0^\infty dt_2\ e^{+i\,(\omega_2+i\gamma_2/2)t_2}\ e^{+i\,(\omega-\omega_1+i\gamma_1/2)t_1}\ \delta(t_1-t_2)\\
&= \int_0^\infty dt\ e^{+i\,(\omega-\omega_{12}+i\gamma_{12}/2)t} = \frac{i}{\omega-\omega_{12}+i\gamma_{12}/2},
\end{aligned} \tag{284}$$

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

$$I(\omega) = I_0\,\frac{\Gamma_{12}^2/4}{\hbar^2\,(\omega-\omega_{12})^2+\Gamma_{12}^2/4}, \tag{285}$$

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.

13 Adiabatic processes

13.1 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_2, 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,

$$H(t)\phi_n(t) = E_n(t)\,\phi_n(t), \tag{286}$$

and solve for

$$i\hbar\,\frac{\partial}{\partial t}\psi = H(t)\,\psi(t). \tag{287}$$

For the solution we use the ansatz

$$\psi(t) = \sum_n c_n(t)\,\phi_n(t)\,e^{i\theta_n(t)}, \tag{288}$$

with

$$i\theta_n(t) = \frac{1}{i\hbar}\int_0^t dt'\;E_n(t'), \tag{289}$$

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

$$\dot{c}_p = -\sum_n \langle\phi_p|\dot{\phi}_n\rangle\,c_n\,e^{i(\theta_n-\theta_p)}. \tag{290}$$

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. 286, $\dot{H}\phi_n = -H\dot{\phi}_n + E_n\dot{\phi}_n + \dot{E}_n\phi_n$, giving

$$\langle\phi_p|\dot{H}|\phi_n\rangle = (E_n - E_p)\,\langle\phi_p|\dot{\phi}_n\rangle. \tag{291}$$

This gives the result

$$\dot{c}_p = -\langle\phi_p|\dot{\phi}_p\rangle\,c_p - \sum_{n\neq p}\frac{\langle\phi_p|\dot{H}|\phi_n\rangle}{E_n - E_p}\,c_n\,e^{i(\theta_n-\theta_p)}. \tag{292}$$

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

$$\psi(t) = e^{i\theta_n(t)}\,e^{i\gamma_n(t)}\,\phi_n(t), \tag{293}$$

where the phase γ_n, defined as

$$\gamma_n(t) \equiv i \int_0^t dt' \; \langle \phi_n | \dot{\phi}_n \rangle, \tag{294}$$

incorparates the effect of the (first) term on the righthandside in Eq. 292. 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*.

13.2 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. 245). 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

$$\chi(t) = \begin{pmatrix} \cos(\alpha/2)\, e^{-i\omega t/2} \left(\cos(\omega_r t) - i\, \frac{(\omega_0 - \omega)}{2\,\omega_r}\, \sin(\omega_r t) \right) \\ \sin(\alpha/2)\, e^{+i\omega t/2} \left(\cos(\omega_r t) - i\, \frac{(\omega_0 + \omega)}{2\,\omega_r}\, \sin(\omega_r t) \right) \end{pmatrix}. \tag{295}$$

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

$$\chi(t) \approx e^{-i\,\omega_0 t/2}\, e^{i(\omega\, \cos\alpha)t/2}\, \chi_+(t). \tag{296}$$

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. 294

$$\gamma_+(t) = i \int_0^t dt' \; \langle \chi_+ | \dot{\chi}_+ \rangle = \tfrac{1}{2}\, (\omega\, \cos\alpha) t.$$

13.3 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

$$\dot{\phi}_n = \boldsymbol{\nabla}_R\,\phi_n\,(\boldsymbol{R}(t)) \cdot \frac{d\boldsymbol{R}}{dt},$$

and the phase is given by

$$\gamma_n(t) = i\int_0^t dt'\,\frac{d\boldsymbol{R}}{dt'}\cdot\langle\phi_n|\boldsymbol{\nabla}_R\,\phi_n\rangle = i\int_{\boldsymbol{R}_i}^{\boldsymbol{R}_f} d\boldsymbol{R}\cdot\langle\phi_n|\boldsymbol{\nabla}_R\,\phi_n\rangle. \tag{297}$$

For a closed contour C in $\boldsymbol{R}$-space, enclosing a surface S, this phase can also be written as a surface integral

$$\gamma_n(t) = i\oint_C d\boldsymbol{R}\cdot\langle\phi_n|\boldsymbol{\nabla}_R\,\phi_n\rangle = i\int_S d\boldsymbol{A}\cdot\boldsymbol{\nabla}_R\times\langle\phi_n|\boldsymbol{\nabla}_R\,\phi_n\rangle. \tag{298}$$

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).

$$\chi_+ = \left(\begin{array}{c} \cos(\theta/2) \\ e^{i\varphi}\,\sin(\theta/2) \end{array}\right).$$

(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

$$\gamma_+(\text{cycle}) = -\frac{1}{2}\int\frac{\hat{\boldsymbol{r}}\cdot d\boldsymbol{a}}{r^2} = -\frac{1}{2}\int d\Omega = -\frac{1}{2}\,\Omega, \tag{299}$$

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

$$r < a: \qquad \boldsymbol{A} = \frac{Br}{2}\,\hat{\boldsymbol{\varphi}} = \left(\frac{-By}{2}, \frac{Bx}{2}, 0\right),$$

$$r > a: \qquad \boldsymbol{A} = \frac{BR^2}{2\,r}\,\hat{\boldsymbol{\varphi}} = \left(\frac{-BR^2\,y}{2\,r^2}, \frac{BR^2\,x}{2\,r^2}, 0\right).$$

In quantum mechanics the field $\boldsymbol{A}$ is very relevant. In fact the Hamiltonian for a charge in an electromagnetic field is described by

$$H = \frac{1}{2m}\left(-i\hbar\boldsymbol{\nabla} - q\,\boldsymbol{A}\right)^2 + q\,\phi. \tag{300}$$

Taking the electric field zero, one sees that the solution is found by looking for eigenstates

$$\left(-i\hbar\boldsymbol{\nabla} - q\boldsymbol{A}\right)\phi_k(\boldsymbol{r}) = \hbar\boldsymbol{k}\,\phi_k(\boldsymbol{r}). \tag{301}$$

Outside of the solenoid, where $\boldsymbol{\nabla}\times\boldsymbol{A} = 0$, the exact solutions involve a line integral

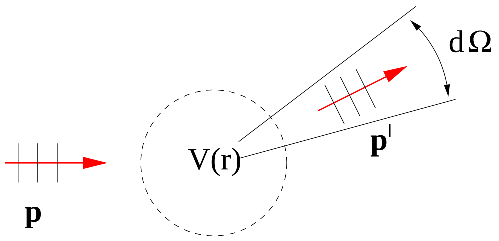
$$\phi_k(\boldsymbol{r};\boldsymbol{A}) = \exp\left(i\,\frac{q}{\hbar}\int_O^{\boldsymbol{r}} d\boldsymbol{s}\cdot A(\boldsymbol{s})\right)\exp\left(i\,\boldsymbol{k}\cdot\boldsymbol{r}\right). \tag{302}$$

This result is in fact nothing else than Berry's phase modifying the plane wave solution. Eq. 300 immediately gives us the gradient of $\phi_k(\boldsymbol{r})$, which can be used in Eq. 297 to get the phase.

14 Scattering theory

14.1 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,

$$n(\theta,\phi)\,d\Omega = |\boldsymbol{j}_{in}|\,d\sigma(\theta,\phi). \tag{303}$$

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.* $\sigma_{\gamma p} \approx 100$ *μb 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.*

14.2 Cross section in Born approximation

We use the result of time-dependent perturbation theory to obtain an expression for the cross section, namely the unperturbed situation is the free case, with as possible solutions, the incoming particle in a plane wave, $\phi_i(\boldsymbol{r}) = \sqrt{\rho}\,\exp\left(i\,\boldsymbol{p}\cdot\boldsymbol{r}/\hbar\right)$, with energy $E = \boldsymbol{p}^2/2m$ and the detected final state, $\phi_f(\boldsymbol{r}) = \sqrt{\rho}\,\exp\left(i\,\boldsymbol{p}'\cdot\boldsymbol{r}/\hbar\right)$, with energy $E' = \boldsymbol{p}'^2/2m$. Note that we allow processes in which the energy of the scattered particle changes. writing $Q \equiv E' - E$ one has $Q = 0$ for an elastic scattering process, an energy release, $Q > 0$, for an exothermic process and energy absorption, $Q < 0$, for an endothermic process. The potential V is a perturbation that can cause transitions between these states. Using Fermi's golden rule, we have for the number of particles with momentum $\boldsymbol{p}'$ (of which the direction with respect to $\boldsymbol{p}$ is given by the angles θ,ϕ),

$$n(\theta,\phi)\,d\Omega = \frac{2\pi}{\hbar}\left[|\langle\phi_f|V|\phi_i\rangle|^2\;\rho(E')\right]_{E'=E+Q}. \tag{304}$$

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,
  $$\boldsymbol{j}(\boldsymbol{r},t) = \frac{\hbar}{2i\,m}\left(\psi^*\,\boldsymbol{\nabla}\psi - (\boldsymbol{\nabla}\psi)^*\psi\right) = \rho\,\frac{\boldsymbol{p}}{m} = \rho\,\boldsymbol{v}. \tag{305}$$
  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
  $$\rho(\boldsymbol{p})\,d^3p = \frac{1}{\rho}\,\frac{d^3p}{(2\pi\hbar)^3}. \tag{306}$$
  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,
  $$\mathbf{1} = \int d^3r\ |\boldsymbol{r}\rangle\,\langle\boldsymbol{r}| = \frac{1}{\rho}\int \frac{d^3p}{(2\pi\hbar)^3}\ |\boldsymbol{p}\rangle\,\langle\boldsymbol{p}|. \tag{307}$$
  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,
  $$\phi_p(\boldsymbol{r}) = \frac{1}{L^{3/2}}\,\exp(i\,\boldsymbol{p}\cdot\boldsymbol{r}/\hbar), \tag{308}$$
  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
  $$\rho(\boldsymbol{p}')d^3p' = \frac{1}{\rho}\,\frac{p'^2}{(2\pi\hbar)^3}\,dp'\,d\Omega' = \frac{1}{\rho}\,\frac{m\,p'}{(2\pi\hbar)^3}\,dE'\,d\Omega' = \rho(E')\,dE'\,d\Omega'. \tag{309}$$

With the flux and density of final states, we get immediately
$$d\sigma(\theta,\phi) = d\Omega'\left(\frac{m}{2\pi\hbar^2}\right)^2\frac{p'}{p}\left|\int d^3r\ \exp\left(\frac{i}{\hbar}\,(\boldsymbol{p}-\boldsymbol{p}')\cdot\boldsymbol{r}\right)\ V(\boldsymbol{r})\right|^2_{E'=E+Q}, \tag{310}$$
or introducing the Fourier transform
$$\tilde{V}(\boldsymbol{k}) = \int d^3r\ V(\boldsymbol{r})\ \exp(i\,\boldsymbol{k}\cdot r), \tag{311}$$
one obtains the following expression for the differential cross section in the socalled *Born approximation*,
$$\frac{d\sigma}{d\Omega'} = \left(\frac{m}{2\pi\hbar^2}\right)^2\frac{p'}{p}\left|\tilde{V}(\boldsymbol{q})\right|^2, \tag{312}$$
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*,
$$\sigma(E) = \int d\Omega\ \frac{d\sigma}{d\Omega}(E,\Omega). \tag{313}$$

Note that in the case of elastic scattering one has $p' = p$ in which case the momentum transfer squared is given by

$$\begin{aligned}\hbar^2 \boldsymbol{q}^2 &= |\boldsymbol{p} - \boldsymbol{p}'|^2 = p^2 + p'^2 + 2\,pp'\,\cos(\theta) \\ &= 2\,p^2(1-\cos\theta) = 4\,p^2\,\sin^2(\theta/2). \end{aligned} \tag{314}$$

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

$$\begin{aligned}\tilde{V}(\boldsymbol{q}) &= \int d^3r\ V(r)\,\exp(i\,\boldsymbol{q}\cdot\boldsymbol{r}) \\ &= 2\pi\int_0^\infty dr \int_{-1}^{1} d\cos\alpha\ r^2 V(r)\,e^{i\,qr\ \cos\alpha} \\ &= \frac{4\pi}{q}\int_0^\infty dr\ rV(r)\,\sin(qr), \end{aligned} \tag{315}$$

only depends on $q = |\boldsymbol{q}|$.

14.3 Applications to various potentials

The square well potential

As a first application consider the square well potential, $V(r) = V_0$ for $r \le a$ and zero elsewhere for sufficiently weak potentials at low energies and small angles ($qa \ll 1$). We will come back to the applicability of the Born approximation in a later section. The Fourier transform is given by

$$\begin{aligned}\tilde{V}(\boldsymbol{q}) &= \frac{4\pi\,V_0}{q}\int_0^a dr\ r\,\sin(qr) \\ &= \frac{4\pi\,V_0}{q^3}\int_0^{qa} dx\ x\,\sin(x) \\ &= \frac{4\pi\,V_0}{q^3}\left[\sin qa - qa\,\cos qa\right] \\ &\xrightarrow{qa\ll 1} \frac{4\pi\,V_0}{q^3}\left[qa - \frac{1}{3!}(qa)^3 - qa + \frac{1}{2!}(qa)^3 + \ldots\right] = \frac{4\pi}{3}\,V_0 a^3, \end{aligned} \tag{316}$$

leading for $E \to 0$ to

$$\frac{d\sigma}{d\Omega} \approx \frac{1}{9}\left(\frac{2m\,V_0\,a^2}{\hbar^2}\right)^2 a^2 \tag{317}$$

The Coulomb potential

The integral

$$\tilde{V}(\boldsymbol{q}) = -\frac{Ze^2}{4\pi\epsilon_0}\,\frac{4\pi}{q}\int_0^\infty dr\ \sin(qr) \tag{318}$$

diverges and we need to consider for instance the screened Coulomb potential, multiplied with $\exp(-\mu r)$. In that case one obtains

$$\begin{aligned}\tilde{V}(\boldsymbol{q}) &= -\frac{Ze^2}{4\pi\epsilon_0}\,\frac{4\pi}{q}\int_0^\infty dr\;\sin(qr)\,e^{-\mu r}\\ &= -\frac{Ze^2}{4\pi\epsilon_0}\,\frac{4\pi}{q}\int_0^\infty dr\;\frac{1}{2i}\left(e^{i(q+i\mu)r}-e^{i(q-i\mu)r}\right)\\ &= -\frac{Ze^2}{\epsilon_0}\,\frac{1}{q^2+\mu^2},\end{aligned} \tag{319}$$

allowing even the limit $\mu \rightarrow 0$ to be taken. Thus

$$\frac{d\sigma}{d\Omega}(E,\theta) = \left(\frac{m}{2\pi\,\hbar^2}\right)^2\left(\frac{Ze^2}{\epsilon_0}\right)^2\frac{1}{q^4} = \left(\frac{Ze^2}{8\pi\,\epsilon_0\,pv}\right)^2\frac{1}{\sin^4(\theta/2)}. \tag{320}$$

This result is known as the Rutherford cross section.

Processes near threshold

If the volume integral over the potential exists, one knows that $\tilde{V}(0)$ is finite and one sees that for small values of the momentum transfer one can write

$$\sigma(E) \;\propto\; \frac{p'}{p} \;=\; \sqrt{\frac{E'}{E}}. \tag{321}$$

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 $E \approx E_{\rm thr}$

$$\sigma(E) \;\propto\; \sqrt{E - E_{\rm thr}}. \tag{322}$$

For an exothermic process (with energy release $Q > 0$) one can scatter for any (positive) energy E and one has near $E \approx 0$

$$\sigma(E) \;\propto\; \frac{1}{\sqrt{E}}. \tag{323}$$

Application to two-particle collisions

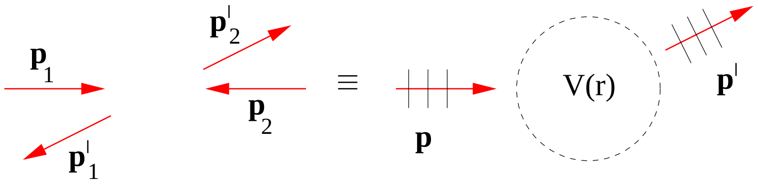
In most applications, the target is not an "external" potential, but rather two particles that collide (*collider experiments*) or one particle that is shot onto another one (*fixed target experiments*). This can in general lead to several possibilities corresponding to several *scattering channels*,

$$\begin{array}{cccl} a+b & \longrightarrow & a+b & \text{(elastic scattering)}\\ & \longrightarrow & c_1+c_2 & \multirow{2}{*}{\Big\}\ \text{(inelastic scattering)}}\\ & \longrightarrow & d_1+d_2+d_3 & \end{array} \tag{324}$$

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

$$\mathscr{I} = \rho\,|\boldsymbol{v}_1 - \boldsymbol{v}_2| = \rho\left|\frac{\boldsymbol{p}_1}{m_1} - \frac{\boldsymbol{p}_2}{m_2}\right| = \rho\left|\frac{\boldsymbol{p}}{\mu}\right|, \tag{325}$$

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.

15 Scattering off a composite system

15.1 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

$$H = H_{\rm system} + H_{\rm e} + V, \tag{326}$$

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

$$\begin{aligned} V(\boldsymbol{q}) &= \int d^3r \int d^3r' \ \exp(-i\,\boldsymbol{k}'\cdot\boldsymbol{r})\,\Phi_B^*(\boldsymbol{r}')\frac{-e^2}{4\pi\,\epsilon_0\,|\boldsymbol{r}-\boldsymbol{r}'|}\,\Phi_A(\boldsymbol{r}')\,exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) \\ &= -\frac{e^2}{4\pi\,\epsilon_0}\int d^3r\ \exp(i\,\boldsymbol{q}\cdot\boldsymbol{r})\int d^3r'\,\frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}, \end{aligned} \tag{327}$$

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

$$\begin{aligned} V(\boldsymbol{q}) &= -\frac{e^2}{4\pi\,\epsilon_0}\int d^3r'\ \exp(i\,\boldsymbol{q}\cdot\boldsymbol{r}')\int d^3r''\ \exp(i\,\boldsymbol{q}\cdot\boldsymbol{r}'')\,\frac{\rho(\boldsymbol{r}')}{r''} \\ &= -\frac{e^2}{4\pi\,\epsilon_0}\,\frac{4\pi}{q^2}\,F(\boldsymbol{q}), \end{aligned} \tag{328}$$

where we have introduced the form factor

$$F(\boldsymbol{q}) = \int d^3r\ \exp(i\,\boldsymbol{q}\cdot\boldsymbol{r})\,\rho(\boldsymbol{r}) \tag{329}$$

which is the Fourier transform of the density. The result for the cross section is

$$\frac{d\sigma}{d\Omega} = \left(\frac{m\,e^2}{2\pi\,\epsilon_0\,\hbar^2\,q^2}\right)^2\frac{p'}{p}\,|F(\boldsymbol{q})|^2\,. \tag{330}$$

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

$$\begin{aligned} \rho_{BA}(\boldsymbol{r}) &= \sum_{j=1}^{Z}\int\prod_{k=1}^{Z} d^3r_k\ \delta^3(\boldsymbol{r}-r_j)\,\Phi_B^*(r_1,\ldots,r_Z)\Phi_A(r_1,\ldots,r_Z) \\ &= Z\int\prod_{k=2}^{Z}\ \Phi_B^*(r,r_2,\ldots,r_Z)\Phi_A(r,r_2,\ldots,r_Z) = Z\,\rho_{BA}(\boldsymbol{r}). \end{aligned} \tag{331}$$

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 $Z^2|\delta_{ab} - F_{ba}|^2$.

15.2 Examples of form factors

Form factors as encountered in the previous section are defined as the Fourier transform of a density,

$$F(\boldsymbol{q}) = \int d^3r \ \exp(i\,\boldsymbol{q}\cdot\boldsymbol{r})\,\rho(\boldsymbol{r}). \tag{332}$$

As before in discussing the potential in momentum space, one has for a spherically symmetric density,

$$F(q) = \frac{4\pi}{q}\int dr\ r\,\rho(r)\ \sin(qr). \tag{333}$$

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

$$F(q) = Q - \frac{1}{6}\,q^2\,\langle r^2\rangle + \ldots, \tag{334}$$

where

$$Q = \int d^3r\ \rho(r), \tag{335}$$

$$\langle r^2\rangle = \int d^3r\ r^2\,\rho(r). \tag{336}$$

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

  $$\rho(r) = \rho_0 \qquad \text{for } x \le R \tag{337}$$

  (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,

  $$F(q) = \frac{3\,j_1(qR)}{qR}, \tag{338}$$

  where

  $$j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}. \tag{339}$$

  Note that

  $$\frac{3\,j_1(x)}{x} \approx 1 - \frac{1}{10}\,x^2 + \ldots, \tag{340}$$

  and, indeed, the charge radius of a uniform distribution is $\langle r^2\rangle = \frac{3}{5}\,R^2$.

- A (normalized) Yukawa distribution
$$\rho(r) = \frac{\mu^2}{4\pi}\,\frac{e^{-\mu r}}{r}, \tag{341}$$
has as form factor
$$F(q) = \frac{\mu^2}{q^2+\mu^2} = \frac{1}{1+q^2/\mu^2}, \tag{342}$$
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
$$\rho(r) = \frac{\mu^3}{8\pi}\,e^{-\mu r}, \tag{343}$$
is simply found by differentiation of the Yukawa form factor with respect to μ,
$$e^{-\mu r} = -\frac{d}{d\mu}\left(\frac{e^{-\mu r}}{r}\right).$$
This gives
$$F(q) = \frac{1}{\left(1+q^2/\mu^2\right)^2}, \tag{344}$$
which is called a *dipole* form factor.

- Finally a normalized Gaussian distribution
$$\rho(r) = \rho_0\,e^{-\frac{1}{2}\,r^2/R^2} \tag{345}$$
has also a Gaussian form factor
$$F(q) = e^{-\frac{1}{2}\,q^2\,R^2}. \tag{346}$$

16 Time-independent scattering solutions

In this section we will attack the scattering of a potential in a different way, namely by solving the Schrödinger equation. The time-independent Schrödinger equation can be rewritten as

$$\left(\boldsymbol{\nabla}^2 + k^2\right)\phi(\boldsymbol{r}) = \frac{2m}{\hbar^2}\,V(\boldsymbol{r})\,\phi(\boldsymbol{r}), \tag{347}$$

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,

$$\left(\boldsymbol{\nabla}^2 + k^2\right)\phi_{\rm hom}(\boldsymbol{r}) = 0. \tag{348}$$

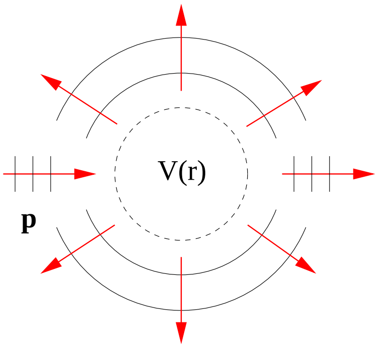
The solutions of the homogeneous equation are well-known, namely the plane waves,

$$\phi_k(\boldsymbol{r}) = \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}),$$

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.*

16.1 Asymptotic behavior and relation to cross section

In order to construct solutions of the Schrödinger equation that describe a scattering process, one wants the appropriate asymptotic behavior, which includes a plane wave part, describing the incoming part and outgoing spherical waves, describing the scattering part, pictorially represented below



We thus require the following asymptotic form,

$$\phi(\boldsymbol{r}) \quad \overset{r\to\infty}{\longrightarrow} \quad \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) + \frac{e^{i\,kr}}{r}\,f(k;\theta,\phi). \tag{349}$$

We have seen in the previous chapter that for $r \to \infty$, this is a solution of the homogeneous equation.

> *It can also simply be checked that the above represents a solution if $r \to \infty$, by inserting it into the homogeneous equation. In order to select the leading part for large r one needs to use that $\boldsymbol{\nabla} f(k;\theta,\phi) \propto 1/r$ and $\boldsymbol{\nabla}^2 f(k;\theta,\phi) \propto 1/r^2$.*

For the asymptotic solution the current corresponding to the first part is given by

$$\boldsymbol{j}_{in} = \frac{\hbar\boldsymbol{k}}{m}, \tag{350}$$

while the second part up to $\mathscr{O}(1/r)$ corresponds with a radially outward directed flux of magnitude

$$j_r = -\frac{i\hbar}{2m}\left[\phi^*\frac{d}{dr}\phi - \left(\frac{d}{dr}\phi^*\right)\phi\right] = \frac{\hbar k}{m}\,\frac{|f(k;\theta,\phi)|^2}{r^2}. \tag{351}$$

From it, one derives the cross section using that

$$|j_{in}|\,d\sigma(\theta,\phi) = n(\theta,\phi)\,d\Omega = j_r\,r^2\,d\Omega, \tag{352}$$

i.e.

$$\frac{d\sigma}{d\Omega} = |f(k;\theta,\phi)|^2. \tag{353}$$

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,

$$\mathscr{I}m\, f_{el}(\theta = 0) = \frac{k}{4\pi}\,\sigma_T, \tag{354}$$

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. 349. 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:

$$\begin{aligned}
&\mathscr{R}e\int_{-1}^{1} dX\;(1+X)\,\frac{e^{i\,kr(1-X)}}{r}\,f \\
&\quad= \mathscr{R}e\int_{-1}^{1} d\left(e^{i\,kr(1-X)}\right)\;\frac{(1+X)f}{-i\,kr^2} \\
&\quad= \mathscr{R}e\left(\frac{2\,f(k;\theta=0)}{-i\,kr^2}\right) - 2\mathscr{R}e\int_{-1}^{1} dX\;\frac{e^{i\,kr(1-X)}}{-i\,kr^2}\,\frac{d}{dX}\left[(1+X)f\right] \\
&\quad= -\frac{2\,\mathscr{I}m\,f(k;\theta=0)}{kr^2} + \mathscr{O}\left(\frac{1}{r^3}\right).
\end{aligned}$$

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.

16.2 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

$$\left(\boldsymbol{\nabla}^2 + k^2\right) G(\boldsymbol{r},\boldsymbol{r}') = -\delta^3(\boldsymbol{r}-\boldsymbol{r}'). \tag{355}$$

> *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

$$G^{(\pm)}(\boldsymbol{r}-\boldsymbol{r}') = -\frac{\exp\left(\pm i\,k|\boldsymbol{r}-\boldsymbol{r}'|\right)}{4\pi\,|\boldsymbol{r}-\boldsymbol{r}'|}. \tag{356}$$

Note that the difference between these two is a solution of the homogeneous equation. In particular $G^{(+)}$ has the correct asymptotic behavior as discussed in the previous section. As an *exact*, but implicit, solution valid for all r, we can write

$$\phi(\boldsymbol{r}) = \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) - \frac{m}{2\pi\,\hbar^2}\int d^3r'\ \frac{\exp\left(+i\,k|\boldsymbol{r}-\boldsymbol{r}'|\right)}{|\boldsymbol{r}-\boldsymbol{r}'|}\,V(\boldsymbol{r}')\,\phi(\boldsymbol{r}'). \tag{357}$$

This result is the desired integral representation of the inhomogenous Schrödinger equation, which has the advantages that the boundary conditions for interpretation as a scattering solution have been built in. It is therefore a good starting point for approximations

The result for $f(k;\theta,\phi)$ is obtained by taking the limit for $r\rightarrow\infty$ in the integral equation, in particular

$$\begin{aligned}
|\boldsymbol{r}-\boldsymbol{r}'| = r\sqrt{1-2\,\frac{\boldsymbol{r}\cdot\boldsymbol{r}'}{r^2}+\frac{r'^2}{r^2}} &\approx r\left[1-\frac{\boldsymbol{r}\cdot\boldsymbol{r}'}{r^2}+\ldots\right],\\
\frac{\exp\left(+i\,k|\boldsymbol{r}-\boldsymbol{r}'|\right)}{|\boldsymbol{r}-\boldsymbol{r}'|} &\approx \frac{e^{i\,kr}}{r}\,\exp\left(i\,\boldsymbol{k}'\cdot\boldsymbol{r}'\right)+\ldots,
\end{aligned}$$

where $\boldsymbol{k}' \equiv k\hat{\boldsymbol{r}}$. This gives

$$\phi^{(+)}_{\rm sc}(\boldsymbol{r}) \quad \stackrel{r\rightarrow\infty}{\longrightarrow} \quad \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r}) - \frac{e^{i\,kr}}{r}\,\frac{m}{2\pi\,\hbar^2}\int d^3r'\ \exp\left(-i\,\boldsymbol{k}'\cdot\boldsymbol{r}'\right)\,V(\boldsymbol{r}')\,\phi^{(+)}_{\rm sc}(\boldsymbol{r}'). \tag{358}$$

and thus the exact expression is

$$f(k;\theta,\phi) = -\frac{m}{2\pi\,\hbar^2}\int d^3r'\ \exp\left(-i\,\boldsymbol{k}'\cdot\boldsymbol{r}'\right)\,V(\boldsymbol{r}')\,\phi^{(+)}_{\rm sc}(\boldsymbol{r}'). \tag{359}$$

16.3 The Born approximation and beyond

The Born approximation is obtained by using perturbation methods, namely to approximate in the above expression $\phi(\boldsymbol{r}') = \exp{(i\,\boldsymbol{k}\cdot\boldsymbol{r}')}$, yielding the result

$$f(k;\theta,\phi) = -\frac{m}{2\pi\,\hbar^2}\int d^3r'\ \exp{(i\,\boldsymbol{q}\cdot\boldsymbol{r}')}\ V(\boldsymbol{r}'), \tag{360}$$

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,*
>
> $$T = V + V\,\tilde{G}\,T, \tag{361}$$
>
> *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*
>
> $$f(k;\theta,\phi) = -\frac{m}{2\pi\,\hbar^2}\,\langle\boldsymbol{p}'|T|\boldsymbol{p}\rangle. \tag{362}$$
>
> *The lowest order (Born approximation) result is the first term in the expansion obtained from Eq. 361,*
>
> $$T = V + V\,\tilde{G}\,V + V\,\tilde{G}\,V\,\tilde{G}\,V + \ldots.$$

To judge the validity of the Born approximation one requires that the scattering term in the wave function is small, i.e.

$$\frac{m}{2\pi\,\hbar^2}\left|\int d^3r'\ \frac{\exp{(i\,k|\boldsymbol{r}-\boldsymbol{r}'|)}}{|\boldsymbol{r}-\boldsymbol{r}'|}\,V(\boldsymbol{r}')\,\phi_{\rm sc}^{(+)}(\boldsymbol{r}')\right| \ll 1. \tag{363}$$

The disturbance of the plane wave is near $r \approx 0$, while for selfconsistency $\phi_{\rm sc}^{(+)}(\boldsymbol{r})$ should be dominantly plane wave, thus

$$\begin{aligned}
\left|\int d^3r'\ \frac{\exp{(i\,kr' + i\,\boldsymbol{k}\cdot\boldsymbol{r}')}}{r'}\,V(\boldsymbol{r}')\right| &\ll \frac{2\pi\,\hbar^2}{m}\\
\left|2\pi\int_{-1}^{1}dX\int dr'\ r'\,e^{i\,kr'(1+X)}\,V(r')\right| &\ll \frac{2\pi\,\hbar^2}{m},\\
\left|\int dr'\ \left(e^{2i\,kr'}-1\right)V(r')\right| &\ll \frac{\hbar^2 k}{m} = \hbar v.
\end{aligned}$$

We see two limits in which the Born approximation is applicable

- Weak potentials with a finite range.
  Starting with the second of the above estimates, we see for a potential with average depth V_0 and range a one has after bringing the absolute value under the integral $V_0\,a^2 \ll \hbar^2/m$, i.e.

  $$V_0 \ll \frac{\hbar^2}{m\,a^2}, \tag{364}$$

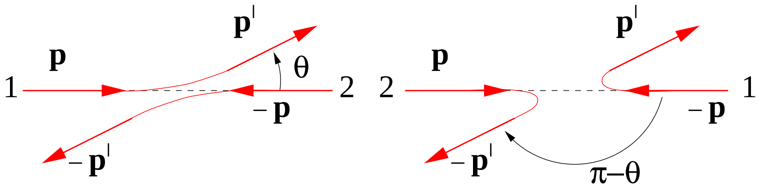
  a condition where an approximately equal sign usually is already ok.

- 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.

$$ka \gg \frac{m\, V_0\, a^2}{\hbar^2} \qquad \text{or} \qquad E \gg \frac{m\, V_0^2\, a^2}{\hbar^2}. \tag{365}$$

16.4 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 $\pi - \theta$,

$$\phi_{12}(\boldsymbol{r}) = e^{i\,kz} + f(k;\theta,\phi)\,\frac{e^{i\,kr}}{r}, \tag{366}$$

$$\phi_{21}(\boldsymbol{r}) = e^{-i\,kz} + f(k;\pi-\theta,\phi+\pi)\,\frac{e^{i\,kr}}{r}, \tag{367}$$

one has the same final state. One should use the appropriately symmetrized or antisymmetrized wave functions, leading to (omitting ϕ-dependence)

$$n(\theta,\phi)\, d\Omega = \frac{\hbar k}{\mu}\,\left|f(k;\theta) \pm f(k;\pi-\theta)\right|^2\, d\Omega$$

In the cross section,

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= \left|f(k;\theta) \pm f(k;\pi-\theta)\right|^2 \\ &= \left|f(k;\theta)\right|^2 + \left|f(k;\pi-\theta)\right|^2 \pm 2\,\mathscr{R}e\left[f^*(k;\theta)\, f(k;\pi-\theta)\right],\end{aligned} \tag{368}$$

the (third) interference term gives rise to oscillations. Note that in order to determine the total cross section one has to integrate over the range $0 \le \theta \le \pi/2$ in order to avoid double counting. Note that the cross sections at angles θ and $\pi - \theta$ are identical. For destructive interference (a minus sign) the cross section is zero at $\theta = 90$ degrees.

For example in the (hypothetical) scattering process of two pions the amplitudes interfere constructively as pions are bosons (spin 0 particles) and the wave function must be symmetric. When scattering two electrons (spin 1/2 particles) off each other the total wave function is antisymmetric, but the symmetry of the scattering solution depends on the spin state. In the spin 0 state (singlet) the spin wave function is antisymmetric, while in the spin 1 state (triplet) the spin wave function is symmetric. Hence

$$\frac{d\sigma_s}{d\Omega} = |f_s(\theta) + f_s(\pi-\theta)|^2, \tag{369}$$

$$\frac{d\sigma_t}{d\Omega} = |f_t(\theta) - f_t(\pi-\theta)|^2, \tag{370}$$

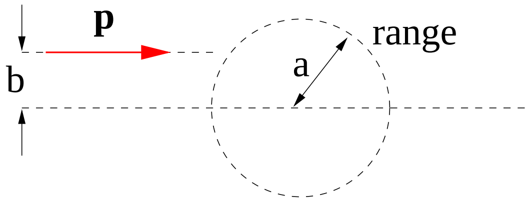
If one scatters unpolarized electrons, the initial state has a probability 1/4 to be in the singlet state, 3/4 to be in the triplet state, thus for a spin-independent potential

$$\frac{d\sigma}{d\Omega} = \frac{1}{4}\frac{d\sigma_s}{d\Omega} + \frac{3}{4}\frac{d\sigma_t}{d\Omega} = |f(k;\theta)|^2 + |f(k;\pi-\theta)|^2 - \mathscr{R}e\left[f(k;\theta)\, f^*(k;\pi-\theta)\right]. \tag{371}$$

17 Partial wave expansion

17.1 Phase shifts

At low energies a particle scattering off a target with impact parameter b has an angular momentum $\hbar\sqrt{\ell(\ell+1)} = p\,b$,



If the potential has a finite range a the angular momenta that are important correspond to $b \le a$. From this we obtain $\hbar\ell \le pa = \hbar ka$ or $\ell \le ka$. 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

$$e^{ikz} = \sum_\ell (2\ell+1)\, i^\ell\, j_\ell(kr)\, P_\ell(\cos\theta). \tag{372}$$

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,

$$f(k;\theta) = \sum_\ell (2\ell+1)\, f_\ell(k)\, P_\ell(\cos\theta). \tag{373}$$

Thus one obtains

$$\phi_{sc}(\boldsymbol{r}) \quad \overset{r\to\infty}{\longrightarrow} \quad \sum_\ell (2\ell+1)\, P_\ell(\cos\theta)\, i^\ell\, \underbrace{\left[j_\ell(kr) + (-i)^\ell\, \frac{e^{i\,kr}}{r}\, f_\ell(k)\right]}_{\phi_{sc}^{(\ell)}(r)}. \tag{374}$$

Rewriting the scattering wave in the following way,

$$\begin{aligned} \phi_{sc}^{(\ell)}(\boldsymbol{r}) \quad &\overset{r\to\infty}{\longrightarrow} \quad \frac{\sin(kr-\ell\pi/2)}{kr} + (-i)^\ell\, \frac{e^{i\,kr}}{r}\, f_\ell(k) \\ &= \quad \frac{1}{2i\,k}\left[-\frac{e^{-i(kr-\ell\pi/2)}}{r} + \frac{e^{i(kr-\ell\pi/2)}}{r}\,(1+2i\,kf_\ell(k))\right], \end{aligned} \tag{375}$$

Conservation of flux tells us that the incoming and outgoing fluxes should be equal in magnitude, i.e.

$$1 + 2i\,kf_\ell(k) \equiv e^{2i\,\delta_\ell(k)}, \tag{376}$$

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

$$f_\ell(k) = \frac{e^{2i\,\delta_\ell(k)} - 1}{2i\,k} = \frac{e^{i\,\delta_\ell(k)}\,\sin\delta_\ell(k)}{k}, \tag{377}$$

and

$$\phi_{sc}^{(\ell)}(\boldsymbol{r}) \quad \overset{r\to\infty}{\longrightarrow} \quad e^{i\,\delta_\ell(k)}\,\frac{\sin(kr-\ell\pi/2+\delta_\ell(k))}{kr}. \tag{378}$$

17.2 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

$$1 + 2i\,k f_\ell(k) \equiv \eta_\ell\, e^{2i\,\delta_\ell(k)}, \tag{379}$$

where η_ℓ is called the *elasticity.* One then has for the elastic cross section

$$\frac{d\sigma_{el}}{d\Omega} = |f(k;\theta)|^2 = 4\pi \sum_{\ell,\ell'} \sqrt{(2\ell+1)(2\ell'+1)}\, f_\ell(k)\, f_{\ell'}(k)\, Y_\ell^{0*}(\theta)\, Y_{\ell'}^0(\theta). \tag{380}$$

Integrating over angles the orthonormality of the Y_ℓ^m's can be used to get

$$\sigma_{el} = \frac{4\pi}{k^2} \sum_\ell (2\ell+1)\, \sin^2\delta_\ell(k) \tag{381}$$

Via the optical theorem, which relates the forward scattering amplitude to the total cross section one finds

$$\sigma_T = \frac{2\pi}{k^2} \sum_\ell (2\ell+1)\,(1 - \eta_\ell\, \cos 2\delta_\ell), \tag{382}$$

which indeed is identical for purely elastic scattering ($\eta_\ell = 1$). The difference is the inelastic cross section,

$$\sigma_{inel} = \frac{\pi}{k^2} \sum_\ell (2\ell+1)\,(1 - \eta_\ell^2). \tag{383}$$

17.3 Application: the phase shift from the potential

The easiest illustration of the calculation of the phase shift is the calculation for a square well, $V(r) = V_0$ for $r \le a$ and zero elsewhere. We immediately know that for $r \ge a$ the solution must be the asymptotic solution. Inside the square well we use the radial Schrödinger equation to get the radial wave function $u(r)$. Thus for

$$\phi_{\ell m}(\boldsymbol{r}) = \frac{u_\ell(r)}{r}\, Y_\ell^m(\theta,\phi), \tag{384}$$

we have

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} + V(r)\right] u_\ell(r) = E\, u_\ell(r). \tag{385}$$

Knowing that $u_\ell(0) = 0$ we obtain for s-waves ($\ell = 0$)

$$\begin{aligned} &r \le a \qquad u(r) = A\,\sin Kr \qquad \text{with } K = \sqrt{\frac{2m}{\hbar^2}\,(E - V_0)}, \\ &r \ge a \qquad u(r) = B\,\sin(kr + \delta_0) \quad \text{with } k = \sqrt{\frac{2m}{\hbar^2}\,E}, \end{aligned}$$

Matching the logarithmic derivative $(du/dr)/u(r)$ at $r = a$ gives

$$\tan(ka + \delta_0) = \frac{k}{K}\,\tan Ka \tag{386}$$

or

$$\begin{aligned}
\tan\delta_0(k) &= \frac{\frac{k}{K}\,\tan Ka - \tan ka}{1 + \frac{k}{K}\,\tan Ka\,\tan ka} && (387)\\
&\xrightarrow{ka \ll 1} \frac{ka\left[\frac{\tan Ka}{Ka} - 1\right]}{1 + (ka)^2\,\frac{\tan Ka}{Ka}}, && (388)\\
&\xrightarrow{Ka \ll 1} ka\left[\frac{\tan Ka}{Ka} - 1\right] \approx \frac{K^2\,a^3}{3}\,k && (389)
\end{aligned}$$

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,

$$\delta_0(k) = a_0\,k + \frac{1}{2}\,r_e\,k^2 + \ldots, \tag{390}$$

have specific names, namely *scattering length* and *effective range*, respectively.