Compendium Quantum Mechanics FYSN17/FMFN01

containing material by

Andreas Wacker, Gunnar Ohlen, Stephanie Reimann and Tineke van den Berg Mathematical Physics

Last revision by Tineke van den Berg

February 23, 2016

ii

Contents

1	For	nulatio	on of Quantum Mechanics	1
	1.1	The ke	et space and the state of a quantum system	2
		1.1.1	Axioms of the ket-space	3
		1.1.2	The dual space and bras	4
		1.1.3	Bases	5
		1.1.4	Physical states and measurement	6
	1.2	Operat	tors and Observables	7
		1.2.1	Matrix representation	8
		1.2.2	The adjoint operator	9
		1.2.3	Hermitian operators	10
		1.2.4	Unitary operators	11
		1.2.5	Physical observables	12
		1.2.6	Relevance of complex phase for quantum states	14
		1.2.7	Continuous spectrum and position operator	15
		1.2.8	Function of an operator	16
		1.2.9	Operator at change of basis [*]	18
		1.2.10	Subspace [*]	18
	1.3	Dynan	nics of Quantum States	19
		1.3.1	Eigenstates of the Hamiltonian	20

		1.3.2 Temporal evolution of expectation values	21
	1.4	Spatial Representation	22
	1.5	Solving the Stationary Schrödinger Equation by Diagonalization $\ .$.	23
2	The	Harmonic Oscillator	27
	2.1	Algebraic Solution by Step Operators	27
	2.2	Eigenfunctions in spatial representation	32
	2.3	Two- and Three-Dimensional Harmonic Oscillator	33
	2.4	Harmonic Oscillator Model for Many-Particle Systems *	36
		2.4.1 Mean-field model and shell structure	36
		2.4.2 Shell structure of the 2D anisotropic harmonic oscillator \therefore	39
		2.4.3 "Magic numbers" in finite fermion systems	41
	2.5	Phonons	44
	2.6	Coherent states [*]	50
3	Ang	gular momentum	53
	3.1	Orbital Angular Momentum and Rotations	53
		3.1.1 Rotations	53
		3.1.2 Spectrum and eigenstates	55
	3.2	Algebra of Angular Momentum	57
		3.2.1 Determining the eigenvalues	58
		3.2.2 Implication for systems with rotational symmetry	60
		3.2.3 Example: Matrix representation of the angular momentum	
		operators	61
	3.3	Spin angular momentum	63
		3.3.1 Algebra and matrix representation	63
		3.3.2 Spin precession in a magnetic field	64

	3.4	Addit	ion of angular momentum	66		
		3.4.1	Sum of angular momenta	66		
		3.4.2	Two spin one-half particles	69		
		3.4.3	Spin-Orbit Coupling and Fine Structure	75		
4	Mag	gnetic	Fields	81		
	4.1	Hamilton Operator in an Electromagnetic Field				
		4.1.1	The electromagnetic potentials	81		
		4.1.2	Main result	82		
		4.1.3	Justification of the Hamiltonian [*] $\ldots \ldots \ldots \ldots \ldots$	84		
	4.2	Zeema	an Effect	85		
	4.3	Landa	u Levels	88		
		4.3.1	Determining the possible $m-\text{values}$ of the states $ N,m\rangle$	89		
5	PEI	RTUR	BATION THEORY	91		
	5.1	Statio	nary Porturbation Theory	02		
				92		
		5.1.1	Non-degenerate case	92 93		
		5.1.1 5.1.2	Non-degenerate case Degenerate case	92 93 95		
		5.1.1 5.1.2 5.1.3	Non-degenerate case Degenerate case Example: The Stark effect	92 93 95 96		
	5.2	5.1.1 5.1.2 5.1.3 Time-	Non-degenerate case Degenerate case Example: The Stark effect dependent Perturbation Theory	 92 93 95 96 99 		
	5.2	5.1.1 5.1.2 5.1.3 Time- 5.2.1	Non-degenerate case Degenerate case Example: The Stark effect dependent Perturbation Theory Interaction picture (Dirac picture)	92 93 95 96 99 100		
	5.2	5.1.1 5.1.2 5.1.3 Time- 5.2.1 5.2.2	Non-degenerate case Degenerate case Example: The Stark effect dependent Perturbation Theory Interaction picture (Dirac picture)	92 93 95 96 99 100 101		
	5.2	5.1.1 5.1.2 5.1.3 Time- 5.2.1 5.2.2 5.2.3	Non-degenerate case Degenerate case Example: The Stark effect dependent Perturbation Theory Interaction picture (Dirac picture) Result Action of a laser pulse on a hydrogen atom	 92 93 95 96 99 100 101 102 		
	5.2	5.1.1 5.1.2 5.1.3 Time- 5.2.1 5.2.2 5.2.3 Fermi	Non-degenerate case	 92 93 95 96 99 100 101 102 103 		
	5.2	5.1.1 5.1.2 5.1.3 Time- 5.2.1 5.2.2 5.2.3 Fermi 5.3.1	Non-degenerate case	 92 93 95 96 99 100 101 102 103 106 		
	5.2	5.1.1 5.1.2 5.1.3 Time- 5.2.1 5.2.2 5.2.3 Fermi 5.3.1 5.3.2	Non-degenerate case	 92 93 95 96 99 100 101 102 103 106 107 		

6	MANY-PARTICLE QUANTUM MECHANICS			113
6.1 Distinguishable Particles			guishable Particles	. 113
		6.1.1	Product states versus entanglement	. 114
		6.1.2	Example: Hydrogen atom as a two particle system $\ . \ . \ .$. 115
	6.2 Identical Particles		cal Particles	. 117
		6.2.1	Symmetry of two-particle states	. 117
		6.2.2	Permutations and extension to N-particle states * $\ . \ . \ .$. 119
	6.3	6.3 Consequences of the Anti-Symmetrization		. 121
		6.3.1	Single-particle operator	. 121
		6.3.2	Two-particle operator	. 121
	6.4	Gener	al Treatment of Many-Body Systems	. 122

Sections marked by a * are auxiliary material which are not addressed in all courses.

Chapter 1

FORMULATION OF QUANTUM MECHANICS

In order to quantify a physical system, a mathematical apparatus has to be identified. In classical mechanics we became used to identify objects with points \mathbf{r}_i in the three-dimensional Euclidean space. These points change in time according to a differential equation $m\ddot{\mathbf{r}} = \mathbf{F}$ (Newton's law, 1687). This guarantees, that for a known initial position and velocity, any possible observable can be precisely determined for all future times. The long success story of this deterministic concept in describing macroscopic processes, such as for example the falling of apples, trajectories of canon balls, or the movement of planets, has essentially formed our conceptual understanding of nature. However, plenty of physical effects, such as the presence of discrete lines in the hydrogen spectrum, as described by Rydbergs law 1888 at Lund University¹ (generalizing earlier work by Balmer) or the Stern-Gerlach experiment² (1922), see Fig. 1.1, indicate, that measurements of physical quantities often provide results, which cannot be explained in terms of classical mechanics.

With the observation by Max Planck in 1900, that the spectrum of black-body radiation can only be understood, if one assumes, that the energy of the radiation is quantized in portions $\hbar\omega$, physicists left the world of classical mechanics. In the

 $^{^{1}\}mathrm{See}$ http://www.fysik.lu.se/english/history/janne-rydberg-and-his-formula/

²See B. Friedrich and D. Herschbach, Physics Today 56(12), 53 (2003) for its historical context



Figure 1.1: Sketch of the Stern-Gerlach experiment (figure by Theresa Knott from Wikipedia). Silver atoms with a magnetic moment μ_B are transversing an inhomogeneous magnetic field which exerts a force depending on the orientation of the magnetic dipole with respect to the field. This provides a splitting of the trajectories of the atoms depending on the z-component of their magnetic moment (the z-direction is chosen as the direction from S to N in the apparatus, which is opposite to the direction of the magnetic field in the center). While one would expect a continuous distribution of deflections for a random orientation of the magnetic moment, only two different deflections are observed.

following 30 years the concepts of quantum mechanics were developed, as we use them today.

Central to its formulation is to use a new mathematical apparatus, where one introduces the complex vector space of *kets* for the description of physical systems. Motivation is for example given in section 1.1 of *Modern Quantum Mechanics* by J.J. Sakurai, drawing on the analogy between the Stern-Gerlach experiment and the polarization of electromagnetic waves.

1.1 The ket space and the state of a quantum system

In order to formulate a physical theory, an appropriate mathematical formalism has to be identified. In the case of Quantum Mechanics this is the algebra of a complex vector space with inner product, which we refer to as *ket-space* here. In the following, the main properties of this mathematical concept are presented with a focus on applications towards quantum mechanics.

1.1.1 Axioms of the ket-space

A vector space contains a class of objects $|\phi\rangle$ (called vectors or, in our case also *kets*) and a field of numbers α (here the complex numbers) satisfying the following axioms:

- The addition of two arbitrary states $|\phi_1\rangle + |\phi_2\rangle = |\phi_3\rangle$ is a further state and $|\phi_1\rangle + |\phi_2\rangle = |\phi_2\rangle + |\phi_1\rangle$ holds (commutative addition).
- The addition of three arbitrary states does not depend on the sequence, i.e. $(|\phi_1\rangle + |\phi_2\rangle) + |\phi_3\rangle = |\phi_1\rangle + (|\phi_2\rangle + |\phi_3\rangle)$ (associativity).
- There exists a null state $|null\rangle$ satisfying $|\phi\rangle + |null\rangle = |\phi\rangle$ for all states $|\phi\rangle$ (it can be shown that there is only one such state).
- For every state |φ⟩ there exists an inverse state |φ̄⟩, so that |φ⟩ + |φ̄⟩ = |null⟩. Conventionally, one writes the addition of an inverse state as subtraction of the state, i.e. |φ₁⟩ |φ₂⟩ = |φ₁⟩ + |φ̄₂⟩.
- A state multiplied by any complex number α ∈ C, α|φ₁⟩ = |φ₂⟩ is another state. In particular 1|φ⟩ = |φ⟩ holds.
- $(\alpha + \beta)|\phi\rangle = \alpha|\phi\rangle + \beta|\phi\rangle$ and $\alpha(|\phi_1\rangle + |\phi_2\rangle) = \alpha|\phi_1\rangle + \alpha|\phi_2\rangle$ for arbitrary states $|\phi_i\rangle$ and complex numbers $\alpha, \beta \in \mathbb{C}$ (distributivity).
- $(\alpha\beta)|\phi\rangle = \alpha(\beta|\phi\rangle)$ for arbitrary states $|\phi\rangle$ and complex numbers α, β .

These axioms of a vector space (as taught in linear algebra) provide the well-known calculation rules used for geometrical vectors in the three-dimensional Euclidean space. However, a major difference (besides the dimensionality) is, that we here deal with a vector space with the field of *complex numbers*, while the Euclidean space is based on the field of real numbers. *This difference is indeed essential for*

the very nature of Quantum Mechanics! On the practical side, it implies a few complications when defining the inner product $\langle \phi_1 | \phi_2 \rangle$ between two states, which now has a complex number as a result. The inner product satisfies the following axioms (see any textbook on linear algebra)

- $\langle \phi | \phi \rangle$ is real and positive, unless for $|\phi\rangle = |null\rangle$, when the result is zero. One usually calls $\sqrt{\langle \phi | \phi \rangle}$ as the *norm* of $|\phi\rangle$.
- $\langle \phi_1 | \phi_2 \rangle = \langle \phi_2 | \phi_1 \rangle^*$
- For $|\phi_3\rangle = \alpha |\phi_1\rangle + \beta |\phi_2\rangle$ the following rules hold: $\langle \phi | \phi_3 \rangle = \alpha \langle \phi | \phi_1 \rangle + \beta \langle \phi | \phi_2 \rangle$, which is intuitive, and $\langle \phi_3 | \phi \rangle = \alpha^* \langle \phi_1 | \phi \rangle + \beta^* \langle \phi_2 | \phi \rangle$, which is often forgotten and leads to common errors!

1.1.2 The dual space and bras

For a given ket $|\phi\rangle$, we can define the mapping

$$|\Psi\rangle \to f_{\phi}(|\Psi\rangle) = \langle \phi|\Psi\rangle$$

which maps each ket onto a complex number. Moreover this mapping $f_{\phi}(|\Psi\rangle)$ is linear as

$$f_{\phi}(\alpha_1|\Psi_1\rangle + \alpha_2|\Psi_2\rangle) = \alpha_1 f_{\phi}(|\Psi_1\rangle) + \alpha_2 f_{\phi}(|\Psi_2\rangle) \quad \text{for all kets } |\Psi_1\rangle, |\Psi_2\rangle \text{ and } \alpha\beta \in \mathbb{C}.$$

In the other direction one can show that each linear mapping from the ket-space into the complex numbers can be written as $\langle \phi | \Psi \rangle$ with an appropriately chosen ket $|\phi\rangle$. Thus there is a one-to-one correspondence of ket states $|\phi\rangle$ and the linear mappings, which themselves form a vector space, called the *dual space*. (In order to show this, one has check at all the axioms for the vector space on page 3 are satisfied for the mappings.) Physicists call these mappings as *bras* and denote them by the symbol $\langle \phi |$, which has now become an identity on its own outside the inner product. However their main usage is in a inner product when $\langle \phi | \Psi \rangle$ is a number. (Phonetically this product is a *bra(c)ket* which is the reason for the choice of names.) As mentioned above there is a one-to-one correspondence between states $|\phi\rangle$ and mappings $\langle \phi |$, which is called *dual correspondence*. Note that from the properties of the inner product we have

$$|\phi\rangle = \alpha_1 |\phi_1\rangle + \alpha_2 |\phi_2\rangle \to \langle \phi| = \alpha_1^* \langle \phi_1| + \alpha_2^* \langle \phi_2| \tag{1.1}$$

Thus some care is needed in determining the dual correspondence of more complicated expressions. (This will be even worse, when operator relations are considered later.)

1.1.3 Bases

A central feature of any vector space is the existence of a basis $\{|a_i\rangle\}$, which is a set of kets. This allows to construct any arbitrary ket $|\phi\rangle$ in a unique way as

$$|\phi\rangle = \sum_{i} c_i |a_i\rangle$$
 with $c_i \in \mathbb{C}$. (1.2)

For a vector space where the inner product is defined, it is possible to construct an orthonormal basis (ON-basis), satisfying $\langle a_j | a_i \rangle = \delta_{ij}$. Note, that there plenty of different ON bases! In the following we will only consider ON bases. Then we can easily determine the expansion coefficients c_i in Eq. (1.2) by multiplication with the bra $\langle a_j |$ from the left, resulting in $c_j = \langle a_j | \phi \rangle$. Inserting this result into Eq. (1.2) provides $|\phi\rangle = \sum_i |a_i\rangle\langle a_i | \phi\rangle$. As this holds for any state $|\phi\rangle$, we identify the

completeness relation
$$\sum_{i} |a_i\rangle\langle a_i| = 1$$
 for any ON basis $\{|a_i\rangle\}$ (1.3)

(sometimes also called *closure relation*) which is a very important tool used in many algebraic transformations.

As a first example we consider

$$\langle \phi | \phi \rangle = \langle \phi | \left(\sum_{i} |a_i\rangle \langle a_i| \right) \phi \rangle = \sum_{i} \left(\langle \phi | a_i \rangle \right) \left(\langle a_i | \phi \rangle \right) = \sum_{i} c_i^* c_i = \sum_{i} |c_i|^2 . \quad (1.4)$$

Thus the norm $\langle \phi | \phi \rangle$ is given by the sum of absolute squares for the expansion coefficients with respect to an ON basis. In particular we find:

$$\langle \phi | \phi \rangle = 1 \quad \Leftrightarrow \quad \sum_i |c_i|^2 = 1.$$

1.1.4 Physical states and measurement

The main concept of quantum mechanics is the following assumption

- 1. Any physical state is identified by a ket $|\Psi\rangle$ with norm 1, i.e., $\langle\Psi|\Psi\rangle = 1$.
- 2. An ideal measurement provides real measurement values α_n associated with physical states $|a_n\rangle$, which form a ON basis of the ket-space.
- 3. For an arbitrary state $|\Psi\rangle$, the *probability* to observe the result α_n in a measurement is given by $P_n = |\langle a_n | \Psi \rangle|^2$.

As $\{|a_n\rangle\}$ is an ON basis we can write

$$|\Psi\rangle = \sum_{n} c_n |a_n\rangle$$
 with $c_n = \langle a_n |\Psi\rangle$ (1.5)

and the normalization of $|\Psi\rangle$ satisfies the requirement that sum of probabilities for all possible outcomes $\sum_{n} P_n = \sum_{n} |c_n|^2 = 1$ is indeed one, where Eq. (1.4) is used.

What happens after the measurement? Once the measurement is performed, and the system was identified to be in the state $|a_n\rangle$, the state vector instantaneously "collapses" to the state $|\Psi\rangle = |a_n\rangle$, corresponding to the newly gained knowledge.

This appearance of probability is quite different from classical physics, where the outcome of any measurement is uniquely defined³. In contrast, fortuitousness is a fundamental property of quantum mechanics.

Example: Stern-Gerlach experiment with magnetic field in z direction, see Fig. 1.1.

This experiment measures the z-component of the magnetic moment μ_z . The measurement provides two possible outcomes $\mu_z = -\mu_B = \alpha_1$ and $\mu_z = \mu_B = \alpha_2$, which correspond to observing the atom in the upper and lower dot on the screen, respectively. These measurements

 $^{^{3}}$ Of course some uncertainty exists in practice but in classical physics one assumes that this always can be reduced by better preparation and measurement techniques.

1.2. OPERATORS AND OBSERVABLES

are associated with the states $|a_1\rangle = |\uparrow_z\rangle$ and $|a_2\rangle = |\downarrow_z\rangle$. If the incoming atom is in the state

$$|\Psi\rangle = \frac{\mathbf{i}}{2}|\uparrow_z\rangle + \frac{\sqrt{3}}{2}|\downarrow_z\rangle \tag{1.6}$$

one detects the atom in the upper dot on the screen (i.e. one measures the value $\mu_z = -\mu_B$ of the magnetic moment) with a probability of 25% and with 75% in the lower dot of the screen (i.e. measuring $\mu_z = \mu_B$). No other values of μ_z can be measured in an ideal apparatus.

Comment on degeneracy: For simplicity, it was assumed that each measurement value α_n corresponds to a single state $|a_n\rangle$. The opposite case is called *degeneracy*, when several different states $|a_{ni}\rangle$ show the same measurement values α_n . These states can be discriminated by a different measurement, with results β_i , so that one needs two (or even more) measurements for a complete characterization. In this case the sums given above have to run over two indices n, i.

Comment on interpretation: The rules given here are sometimes referred to as the Copenhagen interpretation of quantum mechanics. Up to now they are in excellent agreement with experiments.⁴ On the other hand it is fair to say, that these rules appear rather awkward and consequently there is a vivid discussion about 'deeper' interpretations and possible alternate formulations. However none of these attempts has been proven helpful for a better explanation of physical results yet.

1.2 Operators and Observables

An operator \hat{A} transforms kets into other kets. Here we consider only linear operators, which are defined by the property

 $\hat{A}(\alpha|\phi_1\rangle + \beta|\phi_2\rangle) = \alpha \hat{A}|\phi_1\rangle + \beta \hat{A}|\phi_2\rangle \quad \text{for all kets } |\phi_1\rangle, |\phi_2\rangle \text{ and numbers } \alpha\beta \in \mathbb{C} \,.$

Operators can be simply added, providing new operators.

 $^{{}^{4}}A$ highlight was the confirmation of the predicted violation of the Bell inequalities by A. Aspect and his team in 1981/82

The multiplication of operators $\hat{C} = \hat{A}\hat{B}$ is defined as the operator transforming each ket $|\phi\rangle$ into the ket $\hat{A}(\hat{B}|\phi\rangle)$. In contrast to the addition of operators, the multiplication is not commutative. The difference between the two different sequences is a new operator called

commutator:
$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$
 (1.7)

In contrast, the associative law $(\hat{A}\hat{B})\hat{C} = \hat{A}(\hat{B}\hat{C})$ holds for the multiplication of operators.

1.2.1 Matrix representation

As already discussed in section 1.1.3, one can identify any ket $|\phi\rangle$ with a set of numbers c_1, c_2, \ldots , once a basis $\{|a_n\rangle\}$ is defined. In the following we restrict to ON bases and then we find $c_n = \langle a_n | \phi \rangle$.

Similar, we rewrite an arbitrary operator \hat{A} as

$$\hat{A} = \left(\sum_{i} |a_i\rangle\langle a_i|\right) \hat{A}\left(\sum_{j} |a_j\rangle\langle a_j|\right) = \sum_{ij} |a_i\rangle\underbrace{\langle a_i|\hat{A}|a_j\rangle}_{=A_{ij}}\langle a_j|$$
(1.8)

which maps the operator to a complex matrix A_{ij} in the same way as Eq. (1.2) maps a ket to column of indices c_i . Thus, for a given ON-basis $\{|a_i\rangle\}$ we can represent the bras, kets, and operators in the following form:

$$|\phi\rangle \rightarrow \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} \quad \hat{A} \rightarrow \begin{pmatrix} A_{11} & A_{12} & \cdots \\ A_{21} & A_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad \langle\phi| \rightarrow \begin{pmatrix} c_1^* & c_2^* & \cdots \\ c_1^* & c_2^* & \cdots \end{pmatrix}$$

This is called *matrix representation*. Then, for a state $|\phi'\rangle = \sum_i c'_i |a_i\rangle$, we find

$$|\phi'\rangle = \hat{A}|\phi\rangle \iff \begin{pmatrix} c'_1\\c'_2\\\vdots \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} & \cdots\\A_{21} & A_{22} & \cdots\\\vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_1\\c_2\\\vdots \end{pmatrix}$$

and, for $|\varphi\rangle = \sum_i d_i |a_i\rangle$,

$$\langle \varphi | \phi \rangle = \begin{pmatrix} d_1^* & d_2^* & \cdots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}$$

Thus, everything can be calculated using simple matrix multiplications. Remember, however, that

(i) the matrices depend on the basis chosen

(*ii*) the simple relations $A_{ij} = \langle a_i | \hat{A} | a_j \rangle$ only hold for ON bases.

1.2.2 The adjoint operator

Now we want to study how the operators act on bra states. We start with the expression $\langle \phi_2 | \hat{A} | \phi_1 \rangle$ which can be read as the prescription "calculate first the linear transformation $|\phi_1'\rangle = \hat{A} |\phi_1\rangle$ and then the inner product $\langle \phi_2 | \phi_1' \rangle$." Alternatively we may consider the object $\langle \phi_2 | \hat{A}$ as a mapping f of the ket space into the complex numbers. This mapping is obviously linear and according to Sec. 1.1.2 it thus can be associated with some bra $\langle \tilde{\phi}_2 |$ with the suggestive notation $\langle \tilde{\phi}_2 | = \langle \phi_2 | \hat{A}$.

Now we consider the ket $|\tilde{\phi}_2\rangle$ associated with $\langle \tilde{\phi}_2|$ and look for its relation to the original ket $|\phi_2\rangle$. The mapping $|\phi_2\rangle \rightarrow |\tilde{\phi}_2\rangle$ is linear, and therefore it can be associated with a new operator \hat{B} , so that $|\tilde{\phi}_2\rangle = \hat{B}|\phi_2\rangle$. As the new operator \hat{B} is uniquely defined for any operator \hat{A} , one writes $\hat{B} = \hat{A}^{\dagger}$ and it is called the *Hermitian conjugate* or the *adjoint* of \hat{A} . In short:

$$\langle \tilde{\phi} | = \langle \phi | \hat{A}$$
 is the dual correspondence of $| \tilde{\phi} \rangle = \hat{A}^{\dagger} | \phi \rangle$. (1.9)

This concept is very difficult to grasp in the beginning – let us therefore try to describe it again in different and perhaps more simple terms:

According to their definition, operators always act to the right, on the kets. If we now want to think about, how an operator \hat{A} acts on the bra's, we realize that it does it in the same way as its *adjoint* operator \hat{A}^{\dagger} acts on the kets, which is just Eq. (1.9).

If this yet appears un-understandable, try the following: If you want to simplify an expression like $\langle \phi | \hat{A}$, you can replace it by the bra $\langle \tilde{\phi} |$ where the corresponding ket satisfies $|\tilde{\phi}\rangle = \hat{A}^{\dagger} |\phi\rangle$.

With $\langle \tilde{\phi}_2 | = \langle \phi_2 | \hat{A}$, we prove the important relation

$$\langle \phi_2 | \hat{A} | \phi_1 \rangle^* = \langle \tilde{\phi}_2 | \phi_1 \rangle^* = \langle \phi_1 | \tilde{\phi}_2 \rangle = \langle \phi_1 | \hat{A}^{\dagger} | \phi_2 \rangle \tag{1.10}$$

Thus we obtain the matrix representation of the adjoint operator $A_{ij}^{\dagger} = A_{ji}^{*}$, which is just the transposed and complex conjugated matrix of the original operator.

For the operators of the special form $\hat{A} = |\phi_1\rangle\langle\phi_2|$ we may determine the adjoint directly by considering its definition (1.9). We find

$$\langle \tilde{\phi} | = \langle \phi | \hat{A} = \langle \phi | \phi_1 \rangle \langle \phi_2 |$$

and thus the corresponding ket reads by Eq. (1.1)

$$|\tilde{\phi}\rangle = (\langle \phi | \phi_1 \rangle)^* | \phi_2 \rangle = \underbrace{|\phi_2\rangle \langle \phi_1|}_{=\hat{A}^{\dagger}} \phi \rangle$$

where we used the definitions of the inner product. Thus we have the relation

$$(|\phi_1\rangle\langle\phi_2|)^{\dagger} = |\phi_2\rangle\langle\phi_1| \tag{1.11}$$

Furthermore the relations

$$(\hat{A}^{\dagger})^{\dagger} = \hat{A} \tag{1.12}$$

$$(\lambda \hat{A})^{\dagger} = \lambda^* \hat{A}^{\dagger}$$
, where λ is a complex number (1.13)

$$(\hat{A} + \hat{B})^{\dagger} = \hat{A}^{\dagger} + \hat{B}^{\dagger}$$
 (1.14)

$$(\hat{A}\hat{B})^{\dagger} = \hat{B}^{\dagger}\hat{A}^{\dagger} \tag{1.15}$$

hold, which can be easily shown, see the exercises.

1.2.3 Hermitian operators

An operator \hat{A} is called *Hermitian* or *self-adjoint*⁵ if $\hat{A}^{\dagger} = \hat{A}$.

For Hermitian operators \hat{A} the matrix representation satisfies $A_{ij} = A_{ji}^*$ for all ON bases, see Eq. (1.10). Now we know from linear algebra, that such matrices can be diagonalized by a change of basis. Thus:

For Hermitian operators \hat{A} , there exists a special ON basis $\{|a_i\rangle\}$ for which $A_{ij} = \lambda_i \delta_{ij}$ is diagonal. Thus

$$\hat{A} = \sum_{i} \lambda_{i} |a_{i}\rangle \langle a_{i}| \tag{1.16}$$

These states $|a_i\rangle$ are the *eigenstates* and the λ_i are the corresponding *eigenvalues* of the operator \hat{A} .

1.2. OPERATORS AND OBSERVABLES

In practice this basis can be constructed by calculating the eigenvalues and eigencolumns of the matrix A_{ij} in an arbitrary basis.

Regarding the eigenstates of different Hermitian operators \hat{A}, \hat{B} , there is an important theorem about commuting operators proven in textbooks (e.g. section 5.4 of Bransden and Joachain):

 $[\hat{A}, \hat{B}] = 0 \iff \text{ where each ket is eigenstate of}$ (1.17) both operators \hat{A} and \hat{B}

Note that $[\hat{A}, \hat{B}] = 0$ does *not* imply, that any eigenstate of \hat{A} is also an eigenstate of \hat{B} . In general, this only holds for certain sets of eigenstates.

1.2.4 Unitary operators

An operator \hat{U} is called *unitary* if $\hat{U}^{\dagger}\hat{U} = \mathbf{1}$.

This means, that \hat{U}^{\dagger} is the inverse operator for \hat{U} , often written as $\hat{U}^{-1} = \hat{U}^{\dagger}$. An equivalent definition reads

The application of unitary operators does not change the norm of arbitrary kets.

 \hat{U} is unitary $\Leftrightarrow |\phi'\rangle = \hat{U}|\phi\rangle$ implies $\langle \phi'|\phi'\rangle = \langle \phi|\phi\rangle$ for all kets $|\phi\rangle$

The right direction is easily shown by

$$\langle \phi' | \phi' \rangle = \langle \phi | \hat{U}^{\dagger} \hat{U} | \phi \rangle = \langle \phi | \phi \rangle$$

The left direction is slightly more complicated, as one has to show that all matrix elements satisfy $\langle a|\hat{U}^{\dagger}\hat{U}|b\rangle = \langle a|b\rangle$, in order to indentify $\hat{U}^{\dagger}\hat{U} = \mathbf{1}$. For this purpose we consider the state $|\phi_1\rangle = |a\rangle + |b\rangle$. Then $\langle \phi'_1|\phi'_1\rangle = \langle \phi_1|\phi_1\rangle$ implies

$$\langle a'|a'\rangle + \langle a'|b'\rangle + \langle b'|a'\rangle + \langle b'|b'\rangle = \langle a|a\rangle + \langle a|b\rangle + \langle b|a\rangle + \langle b|b\rangle$$

As $\langle a'|a'\rangle = \langle a|a\rangle$ and $\langle b'|b'\rangle = \langle b|b\rangle$, we find

$$\langle a|\hat{U}^{\dagger}\hat{U}|b\rangle + \langle b|\hat{U}^{\dagger}\hat{U}|a\rangle = \langle a|b\rangle + \langle b|a\rangle$$

Considering $|\phi_2\rangle = |a\rangle + i|b\rangle$ provides in the same way

$$\langle a|\hat{U}^{\dagger}\hat{U}|b\rangle - \langle b|\hat{U}^{\dagger}\hat{U}|a\rangle = \langle a|b\rangle - \langle b|a\rangle$$

Adding both equations results in

$$\langle a|\hat{U}^{\dagger}\hat{U}|b\rangle = \langle a|b\rangle$$
 for all kets $|a\rangle, |b\rangle$

and $\hat{U}^{\dagger}\hat{U}$ is the unit operator.

1.2.5 Physical observables

A physical property of a system, that can be observed or measured directly, is called an *observable*. According to the main postulates of quantum mechanics (Sec. 1.1.4) the possible measurement values α_n for an observable are related to specific states $|a_n\rangle$, which form an ON basis of the ket-space. Now we want to associate Hermitian operators with observables. With the definitions of Sec. 1.1.4, and particularly Eq. (1.5), we find the we find the expectation value of the measurement values for an arbitrary quantum state $|\Psi\rangle$

$$\langle \alpha \rangle = \sum_{n} P_{n} \alpha_{n} = \sum_{n} |c_{n}|^{2} \alpha_{n} = \sum_{n} \langle \Psi | a_{n} \rangle \alpha_{n} \langle a_{n} | \Psi \rangle = \langle \Psi | \hat{A} | \Psi \rangle$$
(1.18)

with the Hermitian operator

$$\hat{A} = \sum_{n} |a_n\rangle \alpha_n \langle a_n| \tag{1.19}$$

This suggests to relate observables to the appropriate Hermitian operator. On the other hand, any Hermitian operator can be written in the form (1.19), which allows us to directly identify observables with Hermitian operators. Later we will see many examples such a the position operator, angular momentum, or the Hamilton operator providing the energy of the state. Here we note:

- The real eigenvalues of the Hermitian operator are the possible outcomes of the measurement.
- The eigenstates are states in which the respective outcome of the measurement is obtained with 100% probability.

Example: Operators and expectation values of the Stern Gerlach experiment

According to Eq. (1.19) the operator for the z component of the magnetic moment is

$$\hat{\mu}_z = -\mu_B |\uparrow_z\rangle \langle\uparrow_z| + \mu_B |\downarrow_z\rangle \langle\downarrow_z|$$

with eigenvalues $\pm \mu_B$, where μ_B is the Bohr magneton, the atomic unit of the magnetic moment. The expectation value $\langle \Psi | \hat{\mu}_z | \Psi \rangle$, see Eq. (1.18) is easiest calculated in matrix representation, where we find

$$\langle \Psi | \hat{\mu}_z | \Psi \rangle = \begin{pmatrix} c^*_{\uparrow z} & c^*_{\downarrow z} \end{pmatrix} \begin{pmatrix} -\mu_B & 0 \\ 0 & \mu_B \end{pmatrix} \begin{pmatrix} c_{\uparrow z} \\ c_{\downarrow z} \end{pmatrix}$$

Inserting the state

$$|\Psi\rangle = \frac{\mathrm{i}}{2}|\uparrow_z\rangle + \frac{\sqrt{3}}{2}|\downarrow_z\rangle \to \begin{pmatrix} c_{\uparrow z} \\ c_{\downarrow z} \end{pmatrix} = \begin{pmatrix} \mathrm{i}/2 \\ \sqrt{3}/2 \end{pmatrix}$$

provides $\mu_B/2$ in agreement with adding the probabilities.

Example: Calculation of the eigenstates for the operator $\hat{\mu}_x$

As we will later see, the operator of the magnetic moment in x direction is

 $\hat{\mu}_x = -\mu_B \left(|\uparrow_z\rangle \langle \downarrow_z |+|\downarrow_z\rangle \langle \uparrow_z | \right)$

In matrix notation, with respect to the basis $\{|\uparrow_z\rangle, |\downarrow_z\rangle\}$, this is

$$\hat{\mu}_x \to \begin{pmatrix} 0 & -\mu_B \\ -\mu_B & 0 \end{pmatrix} \tag{1.20}$$

We determine the eigenvalues λ of this matrix by the equation

$$\det \begin{pmatrix} -\lambda & -\mu_B \\ -\mu_B & -\lambda \end{pmatrix} = 0 \Rightarrow \lambda^2 = \mu_B^2$$

and find the eigenvalues $\pm \mu_B$ which are the possible outcomes of a measurement (in this case corresponding to two dots on the screen

after the atoms have passed an inhomogeneous magnetic field in x direction). The corresponding eigen-columns of the matrix are given by

$$\begin{pmatrix} -\lambda & -\mu_B \\ -\mu_B & -\lambda \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

which provide the (normalized) eigenstates as

$$\lambda = -\mu_B \qquad \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} \to \mid \uparrow_x \rangle = \frac{1}{\sqrt{2}} \left(\mid \uparrow_z \rangle + \mid \downarrow_z \rangle \right)$$
$$\lambda = \mu_B \qquad \begin{pmatrix} -1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} \to \mid \downarrow_x \rangle = \frac{1}{\sqrt{2}} \left(-\mid \uparrow_z \rangle + \mid \downarrow_z \rangle \right)$$

Thus measuring the *x*-component of the magnetic moment by an appropriate Stern-Gerlach apparatus projects the system onto one of these two states.

1.2.6 Relevance of complex phase for quantum states

Let us consider the three states

$$\begin{split} |\Psi\rangle &= \frac{\mathrm{i}}{2} |\uparrow_{z}\rangle + \frac{\sqrt{3}}{2} |\downarrow_{z}\rangle \\ |\Psi_{1}\rangle &= \frac{1}{2} |\uparrow_{z}\rangle + \frac{\sqrt{3}}{2} |\downarrow_{z}\rangle \\ |\Psi_{2}\rangle &= \frac{1}{2} |\uparrow_{z}\rangle - \mathrm{i}\frac{\sqrt{3}}{2} |\downarrow_{z}\rangle = -\mathrm{i}|\Psi\rangle \end{split}$$

which all have identical absolute squares $|c_i|^2$ of the expansion coefficients in the basis $\{|\uparrow_z\rangle, |\downarrow_z\rangle\}$. Thus all states have identical probabilities to find the system in $|\uparrow_z\rangle$ and $|\downarrow_z\rangle$. In the same spirit, the average outcome of a measurement of the z component of the magnetic moment is the same. Thus one might conclude that these states represent the same physical system. However for a measurement of the magnetic moment in x direction, a straightforward calculation using the matrix representation (1.20) provides $\langle \Psi | \hat{m}_x | \Psi \rangle = \langle \Psi_2 | \hat{m}_x | \Psi_2 \rangle = 0$ while

1.2. OPERATORS AND OBSERVABLES

 $\langle \Psi_1 | \hat{m}_x | \Psi_1 \rangle = \frac{\sqrt{3}}{2} \mu_B$. Thus the states $|\Psi\rangle$ and $|\Psi_1\rangle$, where the relative phase between the coefficients c_1 and c_2 is different, can be distinguished by an appropriate measurement and do not represent the same physical system.

On the other hand, the relative phase between the coefficients c_1 and c_2 is identical for the states $|\Psi\rangle$ and $|\Psi_2\rangle$, as $|\Psi_2\rangle = e^{i\phi}|\Psi\rangle$, with $\phi = -\pi/2$. Now we show generally that the two states $|\Psi_2\rangle = e^{i\phi}|\Psi\rangle$ and $|\Psi\rangle$ have identical expectation values for all possible operators \hat{A} . Indeed

$$\langle \Psi_2 | \hat{A} | \Psi_2 \rangle = \langle \Psi | e^{-i\phi} \hat{A} e^{i\phi} | \Psi \rangle = e^{-i\phi} e^{i\phi} \langle \Psi | \hat{A} | \Psi \rangle = \langle \Psi | \hat{A} | \Psi \rangle$$

Thus, two states $|\Psi\rangle$ and $|\Psi_2\rangle$, satisfying $|\Psi_2\rangle = e^{i\phi}|\Psi\rangle$, have identical properties for all possible measurements and cannot be distinguished.

1.2.7 Continuous spectrum and position operator

Many observables, such as a position x in space, are continuous variables. Describing a physical observable there is an operator \hat{x} with eigenvalues x and corresponding eigenstates $|x\rangle$. Thus

$$\hat{x}|x\rangle = x|x\rangle \tag{1.21}$$

In contrast to the states $|a_n\rangle$ considered before (which could be numbered with natural numbers n = 1, 2, 3...), continuous variables cannot be described by sums. While a thorough description is mathematically complicated, we state here only that the inner product between the basis state reads

$$\langle x|x'\rangle = \delta(x-x') \tag{1.22}$$

where $\delta(x - x')$ is Dirac's delta function and the completeness relation (1.3) becomes

$$\int \mathrm{d}x |x\rangle \langle x| = \mathbf{1} \ . \tag{1.23}$$

For an arbitrary quantum state we may write

$$|\Psi\rangle = \int \mathrm{d}x |x\rangle \langle x|\Psi\rangle$$

and $|\langle x|\Psi\rangle|^2 \Delta x$ is the probability to observe the quantum system in the interval $(x, x + \Delta x)$. With other words, $|\langle x|\Psi\rangle|^2$ is the probability density. Thus, we can identify the well-known wavefunction as

$$\Psi(x) = \langle x | \Psi \rangle \tag{1.24}$$

which is just the representation of the kets in the basis of position eigenstates, also called *spatial representation*.

Let us assume that the position operators of different spatial directions commute with each other, i.e.,

$$[\hat{x}, \hat{y}] = [\hat{x}, \hat{z}] = [\hat{z}, \hat{y}] = 0 .$$
(1.25)

We then can, according to (1.17), find a set of basis states, labeled $|x, y, z\rangle$, which are eigenstates of all three spatial operators, with respective eigenvalues x, y, z. These are usually combined to the spatial vector **r**. In this way, we obtain $\Psi(\mathbf{r}) = \langle x, y, z | \Psi \rangle$ in the three-dimensional space. Then the inner product between two states reads

$$\langle \Psi_1 | \Psi_2 \rangle = \int \mathrm{d}^3 r \langle \Psi_1 | \mathbf{r} \rangle \langle \mathbf{r} | \Psi_2 \rangle = \int \mathrm{d}^3 r \, \Psi_1^*(\mathbf{r}) \Psi_2(\mathbf{r})$$

where we inserted the completeness relation (1.23)

1.2.8 Function of an operator

Frequently we use functions $f(\hat{A})$ of an operator \hat{A} . The simplest example is $f(x) = x^2$ and then we define $f(\hat{A}) = \hat{A}^2$ as the operator given by the product $\hat{A}\hat{A}$. For powers of operators the important relation

$$[\hat{B}, \hat{A}^n] = n[\hat{B}, \hat{A}]\hat{A}^{n-1}$$
 if $[[\hat{B}, \hat{A}], \hat{A}] = 0$ (1.26)

holds, as shown in the exercises. More complicated functions f(x) can generally be defined via the Taylor expansion as

$$f(\hat{A}) = \sum_{n=0}^{\infty} \frac{f_n}{n!} \hat{A}^n \quad \text{for the function } f(x) = \sum_{n=0}^{\infty} \frac{f_n}{n!} x^n \tag{1.27}$$

Example: Show that

$$[\hat{B}, f(\hat{A})] = [\hat{B}, \hat{A}]f'(\hat{A}) \text{ if } [[\hat{B}, \hat{A}], \hat{A}] = 0$$
 (1.28)

According to the definition for functions of operators we have

$$\begin{split} [\hat{B}, f(\hat{A})] &= \sum_{n=0}^{\infty} \frac{f_n}{n!} [\hat{B}, \hat{A}^n] = \sum_{n=0}^{\infty} \frac{f_n}{n!} n[\hat{B}, \hat{A}] \hat{A}^{n-1} \\ &= [\hat{B}, \hat{A}] \sum_{n=1}^{\infty} \frac{f_n}{(n-1)!} \hat{A}^{n-1} = [\hat{B}, \hat{A}] f'(\hat{A}) \end{split}$$

where Eq. (1.26) was used and we identified $f'(x) = \sum_{n=1}^{\infty} \frac{f_n}{(n-1)!} x^{n-1}$, which follows directly from the derivative of Taylor expansions. A particular important application is $[\hat{p}, f(\hat{x})] = \frac{\hbar}{i} f'(\hat{x})$ which will be used later.

There is an alternative definition for the function of Hermitian operators \hat{A} . As discussed in Sec. 1.2.3 an ON basis of eigenstates $|a_n\rangle$ with eigenvalues λ_n exists for such operators. Then we can define the function as

$$f(\hat{A}) = \sum_{n} |a_n\rangle f(\lambda_n) \langle a_n| . \qquad (1.29)$$

which can be shown to agree with the definition (1.29)

Example: Show that

$$\hat{U} = e^{i\hat{A}}$$
 is unitary for a Hermitian operator \hat{A} (1.30)

For Hermitian operators \hat{A} , the second definition provides

$$\mathrm{e}^{\mathrm{i}\hat{A}} = \sum_{n} |a_n\rangle \mathrm{e}^{\mathrm{i}\lambda_n} \langle a_n|$$

where the kets $|a_n\rangle$ are the eigenstates of \hat{A} with eigenvalues λ_n . Eqs. (1.11,1.13,1.14) provide directly

$$\hat{U}^{\dagger} = \sum_{n} |a_n\rangle \mathrm{e}^{-\mathrm{i}\lambda_n} \langle a_n| = \mathrm{e}^{-\mathrm{i}\hat{A}}$$

Now we consider

$$\hat{U}\hat{U}^{\dagger} = \left(\sum_{n} |a_{n}\rangle e^{i\lambda_{n}} \langle a_{n}|\right) \left(\sum_{m} |a_{m}\rangle e^{-i\lambda_{m}} \langle a_{m}|\right)$$
$$= \sum_{nm} |a_{n}\rangle e^{i\lambda_{n}} \underbrace{\langle a_{n}|a_{m}\rangle}_{=\delta_{nm}} e^{-i\lambda_{m}} \langle a_{m}| = \sum_{n} |a_{n}\rangle \langle a_{n}| = \mathbf{1}$$

Thus \hat{U} is unitary.

1.2.9 Operator at change of basis^{*}

Let $\{|a_i\rangle\}$ and $\{|b_i\rangle\}$ be two different ON basis sets. Then, the linear operator

$$\hat{U} = \sum_{i} |b_i\rangle\langle a_i| \tag{1.31}$$

satisfies $\hat{U}|a_i\rangle = \sum_j |b_j\rangle \langle a_j|a_i\rangle = |b_i\rangle$ for all basis states and thus provides the basis transformation. From Eq. (1.11) we find

$$\hat{U}^{\dagger} = \sum_{i} |a_i\rangle \langle b_i| ,$$

and thus

$$\hat{U}\hat{U}^{\dagger} = \sum_{ij} |b_i\rangle \underbrace{\langle a_i | a_j \rangle}_{\delta_{ij}} \langle b_i | = \sum_j |b_j\rangle \langle b_j | = 1$$

which shows that \hat{U} is unitary.

1.2.10 Subspace*

The ket space (or Hilbert space) is typically of infinite dimension and thus the the matrices (A_{ij}) are infinite-dimensional. Often, however, and in particular for computational purposes, we need to deal with *finite* matrices. The easiest way to achieve this, is to approximate the Hilbert space with a *finite-dimensional subspace* \mathcal{M} , spanned by a finite orthonormal set of kets $\{|u_i\rangle\}_{i=1}^N$. Then this subspace contains all kets, which can be written as

$$|\nu\rangle_{finite} = \sum_{i=1}^{N} a_i |u_i\rangle$$
.

1.3. DYNAMICS OF QUANTUM STATES

We can define a so-called *projector* \hat{P} (or projection operator) as

$$\hat{P} = \sum_{i=1}^{N} |u_i\rangle\langle u_i| \tag{1.32}$$

such that for all states $|\nu\rangle$ of the Hilbert space

$$|\nu\rangle_{finite} = \hat{P}|\nu\rangle$$
.

is in \mathcal{M} . This operator gives the "orthogonal projection" of the space \mathcal{H} on \mathcal{M} . A subspace \mathcal{M} is said to be invariant with respect to an operator \hat{A} , if

$$|u\rangle \in \mathcal{M} \qquad \Rightarrow \qquad \hat{A}|u\rangle \in \mathcal{M}$$

Then, there are no matrix elements between elements (i.e., vectors) inside and outside of \mathcal{M} :

$$|\nu\rangle \notin \mathcal{M} \quad \Rightarrow \quad \langle \nu | \hat{A} | u \rangle = 0$$

The matrix representing \hat{A} then consists of *blocks* along the diagonal:

This notice has much practical importance for calculations: Often, you may *use* symmetries to transform the matrix into such a block-diagonal form. Each block can then be treated separately, which in many cases can reduce the dimensionality of the problem very drastically.

1.3 Dynamics of Quantum States

The time-dependence of the quantum state is given by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle ,$$
 (1.34)

with the Hamilton operator \hat{H} that accounts for the physical properties of the system.

For particles with mass m moving in the potential V(x, y, z), for example, the Hamilton operator is

$$\hat{H} = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} + V(\hat{r}_x, \hat{r}_y, \hat{r}_z)$$
(1.35)

where we slightly changed the notation using $\hat{r}_x = \hat{x}, \hat{r}_y = \hat{y}, \hat{r}_z = \hat{z}$. Here the momentum operators \hat{p}_j and spatial operators \hat{r}_j satisfy the commutation relations

$$[\hat{p}_j, \hat{p}_k] = 0, \quad [\hat{r}_j, \hat{r}_k] = 0, \quad \text{and} \quad [\hat{p}_j, \hat{x}_k] = \frac{\hbar}{i} \delta_{jk} .$$
 (1.36)

To simplify the notation one conventionally defines

$$\hat{\mathbf{p}} = \hat{p}_x \mathbf{e}_x + \hat{p}_y \mathbf{e}_y + \hat{p}_z \mathbf{e}_z$$
 and $\hat{\mathbf{r}} = \hat{x} \mathbf{e}_x + \hat{y} \mathbf{e}_y + \hat{z} \mathbf{e}_z$

and the resulting expressions look pretty much as in classical mechanics. Note however, that $\hat{\mathbf{r}}$ is an operator in our ket-space and not a classical position. In this context $V(\hat{\mathbf{r}})$ is the function of an operator in the spirit of Section 1.2.8.

Formally, the structure of the Hamilton operator can be motivated from the theory of analytical mechanics, where many of the concepts originate from. The precise meaning of momentum in more complicated situations must be clarified separately. This will become of relavance for the magnetic field as discussed in Sec. 4.1. Furthermore, the symmetry properties of space are related to the commutation relations for space and momentum, see, e.g. section 1.6 and chapter 2 of of the textbook *Modern Quantum Mechanics* by J.J Sakurai.

1.3.1 Eigenstates of the Hamiltonian

The eigenstates $|\varphi_n\rangle$ of the (time-independent) Hamilton-operator are determined by the stationary Schrödinger equation

$$\hat{H}|\varphi_n\rangle = E_n|\varphi_n\rangle. \tag{1.37}$$

The eigenvalues E_n are the energies which can be measured. Expanding an arbitrary state $|\Psi(t)\rangle$ in these eigenstates $|\Psi(t)\rangle = \sum_n c_n(t)|\varphi_n\rangle$, Eq. (1.34) provides

$$i\hbar \sum_{n} \dot{c}_{n}(t) |\varphi_{n}\rangle = \sum_{n} c_{n}(t) E_{n} |\varphi_{n}\rangle .$$

1.3. DYNAMICS OF QUANTUM STATES

Multiplying by $\langle \varphi_n |$ gives

$$i\hbar\dot{c}_n(t) = c_n(t)E_n \Rightarrow c_n(t) = c_n(0)e^{-iE_nt/\hbar}$$
(1.38)

which constitutes a complete solution of the time dependence for the quantum state $|\Psi(t)\rangle$ for a given initial condition at t = 0.

1.3.2 Temporal evolution of expectation values

If the system is in a quantum state $|\Psi\rangle$ we can evaluate expectation values of arbitrary operators \hat{A} in the form $\langle \Psi | \hat{A} | \Psi \rangle$. These are changing in time as

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle \Psi | \hat{A} | \Psi \rangle = \left(\frac{\partial}{\partial t} \langle \Psi | \right) \hat{A} | \Psi \rangle + \langle \Psi | \left(\frac{\partial}{\partial t} \hat{A} \right) | \Psi \rangle + \langle \Psi | \hat{A} \left(\frac{\partial}{\partial t} | \Psi \rangle \right)$$

Using the Schrödinger equation $\frac{\partial}{\partial t}|\Psi\rangle = \frac{1}{i\hbar}\hat{H}|\Psi\rangle$ and its dual correspondence $\frac{\partial}{\partial t}\langle\Psi| = -\frac{1}{i\hbar}\langle\Psi|\hat{H}^{\dagger}$, as well as the Hermiticity of \hat{H} we find

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle \Psi | \hat{A} | \Psi \rangle = \frac{1}{\mathrm{i}\hbar} \left(- \langle \Psi | \hat{H} \hat{A} | \Psi \rangle + \langle \Psi | \hat{A} \hat{H} | \Psi \rangle \right) + \langle \Psi | \left(\frac{\partial}{\partial t} \hat{A} \right) | \Psi \rangle$$

This provides the important relation

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle \Psi | \hat{A} | \Psi \rangle = \frac{\mathrm{i}}{\hbar} \langle \Psi | [\hat{H}, \hat{A}] | \Psi \rangle + \langle \Psi | \frac{\partial \hat{A}}{\partial t} | \Psi \rangle$$
(1.39)

Thus the time dependence of the expectation value of an operator is given by the expectation value of the commutator with the Hamilton operator as well as a possible explicit time-dependence of the corresponding operator.

Example: Expectation values of the harmonic oscillator

Consider a mass m, which is fixed to a spring exerting the force -fx for the elongation x from the point of rest. The corresponding potential is $V(x) = fx^2/2$ and we find the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{f}{2}\hat{x}^2$$

Using
$$[\hat{p}^2, \hat{x}] = 2\hat{p}\hbar/i$$
 and $[\hat{x}^2, \hat{p}] = -2\hat{x}\hbar/i$, see Eq. (1.26), we find

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\Psi|\hat{x}|\Psi\rangle = \frac{\mathrm{i}}{\hbar}\langle\Psi|[\hat{H}, \hat{x}]|\Psi\rangle = \frac{1}{m}\langle\Psi|\hat{p}|\Psi\rangle$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\Psi|\hat{p}|\Psi\rangle = \frac{\mathrm{i}}{\hbar}\langle\Psi|[\hat{H}, \hat{p}]|\Psi\rangle = -f\langle\Psi|\hat{x}|\Psi\rangle$$

Thus the expectation values satisfy the same equations of motion as the momentum and position of a classical particle, which is called the correspondence principle or Ehrenfest theorem. (More generally one finds $\frac{d}{dt}\langle\Psi|p|\Psi\rangle = \langle\Psi|F(\hat{x})|\Psi\rangle$ where F(x) is the force on the particle at position x.)

1.4 Spatial Representation

In spatial representation, we use the eigenstates $|x\rangle$ of the space operator as basis elements. Then the operators \hat{x} and \hat{p}_x can be written in the form of the matrices

$$\langle x|\hat{x}|x'\rangle = x\delta(x-x')$$
 and $\langle x|\hat{p}_x|x'\rangle = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}\delta(x-x')$. (1.40)

The first part follows directly from equations (1.21,1.22). The second part is much more difficult to prove⁶. Here we show, that the given marix elements provide the key commutation relation $[\hat{p}_x, \hat{x}] = \frac{\hbar}{i}$ in spatial representation, which at least demonstrates consistency. For this purpose we consider

$$\begin{aligned} \langle x|[\hat{p}_{x},\hat{x}]|\phi\rangle &= \int \mathrm{d}x' \int \mathrm{d}x'' \left(\langle x|\hat{p}_{x}|x'\rangle \langle x'|\hat{x}|x''\rangle \langle x''|\phi\rangle - \langle x|\hat{x}|x'\rangle \langle x'|\hat{p}_{x}|x''\rangle \langle x''|\phi\rangle \right) \\ &= \int \mathrm{d}x' \int \mathrm{d}x'' \left(\frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial x} \delta(x-x')x'\delta(x'-x'')\phi(x'') - x\delta(x-x')\frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial x'}\delta(x'-x'')\phi(x'') \right) \\ &= \int \mathrm{d}x' \left(\frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial x} \delta(x-x')x'\phi(x') - x\delta(x-x')\frac{\hbar}{\mathrm{i}}\phi'(x') \right) \\ &= \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial x} \left(x\phi(x) \right) - x\frac{\hbar}{\mathrm{i}}\phi'(x) = \frac{\hbar}{\mathrm{i}}\phi(x) \end{aligned}$$

where $\phi'(x)$ is a shorthand for the derivative of $\phi(x)$ with respect to x. Thus we find $\langle x | [\hat{p}_x, \hat{x}] | \phi \rangle = \frac{\hbar}{i} \langle x | \phi \rangle$ as it should be.

 $^{^{6}}$ In the book J.J. Sakurai and J. Napolitano *Moden Quantum Mechanics* this is shown by using the property of momentum to be the generator of translations

Correspondingly, in three dimensions the spatial representation of the operators $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ is given by

$$\langle \mathbf{r} | \hat{\mathbf{r}} | \mathbf{r}' \rangle = \mathbf{r} \delta(\mathbf{r} - \mathbf{r}') \text{ and } \langle \mathbf{r} | \hat{\mathbf{p}} | \mathbf{r}' \rangle = \frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}} \delta(\mathbf{r} - \mathbf{r}')$$
(1.41)

Multiplying Eq. (1.34) with $\langle \mathbf{r} |$ and inserting (1.23) for all three spatial coordinates, the Schrödinger equation becomes

$$i\hbar \frac{\partial}{\partial t} \underbrace{\langle \mathbf{r} | \Psi \rangle}_{=\Psi(\mathbf{r},t)} = \int d^3 r' \langle \mathbf{r} | \hat{H} | \mathbf{r}' \rangle \underbrace{\langle \mathbf{r}' | \Psi \rangle}_{=\Psi(\mathbf{r}',t)}$$

Now Eq. (1.41) shows that the basic operators $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ become diagonal in space. Thus, arbitrary operators of the form $f(\hat{\mathbf{r}}, \hat{\mathbf{p}})$ can be written as

$$\langle \mathbf{r} | f(\hat{\mathbf{r}}, \hat{\mathbf{p}}) | \mathbf{r}' \rangle = \underbrace{f\left(\mathbf{r}, \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial \mathbf{r}}\right)}_{=\hat{f}^{\mathrm{SR}}} \delta(\mathbf{r} - \mathbf{r}')$$

which defines the spatial representation \hat{f}^{SR} of an arbitrary operator \hat{f} , which can be expressed in terms of the canonical variables $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$. For the Hamiltonian (1.35) this provides the common Schrödinger equation in spatial representation⁷

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t)=\hat{H}^{\mathrm{SR}}\Psi(\mathbf{r},t)\quad\text{with}\quad\hat{H}^{\mathrm{SR}}=-\frac{\hbar^2}{2m_e}\nabla^2+V(\mathbf{r})$$

which has been used in the elementary quantum mechanics you studied in previous courses.

1.5 Solving the Stationary Schrödinger Equation by Diagonalization

Consider the stationary Schrödinger equation

$$\hat{H}|\varphi_k\rangle = E_k|\varphi_k\rangle$$
.

⁷Note that it is possible to define more general effective Hamilton operators, which are not diagonal in space (a common example occurs in the Hartree-Fock approximation). Then, the \mathbf{r}' -integral has to be kept.

For a given Hamilton operator \hat{H} , the eigenvalues E_k and eigenstates $|\varphi_k\rangle$ are not known. To solve the problem, we may begin by expanding the state $|\varphi_k\rangle$ in a basis $\{|a_i\rangle\}$,

$$|\varphi_k\rangle = \sum_i C_{ki} |a_i\rangle$$
,

where the $\{|a_i\rangle\}$ form a complete orthonormal set (ON base) in the Hilbert space \mathcal{H} . We recall that

$$C_{ki} = \langle a_i | \varphi_k \rangle$$
 since $|\varphi_k \rangle = \sum_{i = 1}^{i} |a_i \rangle \langle a_i | \varphi_k \rangle$

Here, the summation index in principle runs from i = 1 to ∞ . For almost all practical purposes, one needs to restrict the set of basis functions to be finite, which requires the consideration of a subspace as addressed in section 1.2.10. The expansion for $|\varphi_k\rangle$ can now be inserted back into the Schrödinger equation:

$$\hat{H}\sum_{i} C_{ki} |a_i\rangle = E_k \sum_{i} C_{ki} |a_i\rangle$$

Multiplying by $\langle a_j |$ from left, we obtain for each $j \sum_i C_{ki} \langle a_j | \hat{H} | a_i \rangle = E_k C_{kj}$, or

$$\sum_{i} C_{ki} (H_{ji} - \delta_{ji} E_k) = 0 \quad \text{with the matrix} \quad H_{ji} = \langle a_j | \hat{H} | a_i \rangle \tag{1.42}$$

It can also be written in matrix form:

$$\begin{pmatrix} H_{11} - E_k & H_{12} & H_{13} & . \\ H_{21} & H_{22} - E_k & H_{23} & . \\ H_{31} & H_{32} & H_{23} - E_k & . \\ . & . & . & . \\ . & . & . & . \end{pmatrix} \begin{pmatrix} C_{k1} \\ C_{k2} \\ C_{k3} \\ . \\ . \\ . \\ . \end{pmatrix} = 0 \qquad (1.43)$$

The size of the matrix is then naturally $N \times N$, i.e. it (trivially) is determined by the truncation of the basis. This leaves us with N coupled linear equations. This can be solved, and we find the non-trivial solutions from the so-called "secular equation",

$$\Leftrightarrow \qquad Det(H_{ji} - \delta_{ji}E_k) = 0$$

which gives us the N eigenvalues E_k through the possible roots of this equation. For a specific E_k , one then obtains a specific set of coefficients $(C_{k,i})$. This gives the eigenvector

$$\begin{pmatrix} C_{k1} \\ C_{k2} \\ C_{k3} \\ \vdots \\ \vdots \\ \vdots \end{pmatrix}$$

associated to the k^{th} eigenstate.

If the dimensionality of the problem is small, as for example with N = 3 or N = 4 basis states, such diagonalization can be done "by hand", and in the exercises we will treat some examples. For bigger matrix dimensions, however, one needs to use numerical routines on a computer.

If the matrix is diagonal from the start, then the problem is trivial: The H_{ii} (diagonal elements) are the energy eigenvalues, and $C_{ki} = \delta_{k,i}$

Some important remarks

• Choice of basis functions

In principle, any ON set can be chosen as a base. However, the better the choice, the easier is the task!

Basis functions that are close to the exact ones, are the best. Then, many of the C_{ki} 's are very small, and one may truncate very efficiently. The calculation of the matrix elements can often be troublesome, since it involves integrals. Always choose a "nice" basis, that is well-behaving and can be integrated - smooth functions that do not oscillate too wildly will do a good job, and you do not want to have any divergent terms...

• Truncation of the basis

In most cases, you will need to *truncate* rather severely in order for the problem to fit into the computer memory. Always assure, that your final result does not depend on the truncation; i.e., check *convergence* of the

crucial quantities (such as for example the energies) with respect to the basis size! When you choose a larger basis, your results are not supposed to change too much.

• Choice of diagonalization routines

For the *diagonalization* of the matrix on the computer, many different numerical routines exist! The structure of your matrix determines which one is the best. Check, whether the matrix is sparse, block-diagonal *etc.*

Finally, a comment on the relation to classical mechanics - Diagonalization in a sense corresponds to a transformation to the axes of inertia in classical mechanics.

Chapter 2

The Harmonic Oscillator

The harmonic oscillator is a very important example both in classical and quantum physics. In the basic course we used an elementary method based on Schrödinger equation in differential form. In this chapter we will use a more advanced method based so on called step operators. Similar operator methods will frequently be used in later chapters. Sections with a * will only be treated loosely.

2.1 Algebraic Solution by Step Operators

We first study the one dimensional case. The Hamiltonian is

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 \hat{x}^2$$
(2.1)

If we introduce dimensionless operators

$$\hat{P} = \frac{1}{\sqrt{m\hbar\omega}}\hat{p}, \quad \hat{X} = \sqrt{\frac{m\omega}{\hbar}}\hat{x}$$
 (2.2)

the Hamiltonian becomes

$$\hat{H} = \frac{1}{2}\hbar\omega(\hat{P}^2 + \hat{X}^2)$$
(2.3)

If \hat{P} and \hat{X} had not been operators then \hat{H} could have been factorized: $H = \frac{1}{2}\hbar\omega(X - iP)(X + iP)$. This is not possible because the operators do not commute. Let us in any case introduce operators \hat{a} and \hat{a}^{\dagger} :

$$\hat{a} = \frac{1}{\sqrt{2}}(\hat{X} + i\hat{P}), \quad \hat{a}^{\dagger} = \frac{1}{\sqrt{2}}(\hat{X} - i\hat{P})$$
 (2.4)

It is important to remember that these operators are not Hermitian. The following commutator relations are useful

$$[\hat{X}, \hat{P}] = \sqrt{\frac{m\omega}{\hbar}} \frac{1}{\sqrt{m\hbar\omega}} [\hat{x}, \hat{p}] = \frac{1}{\hbar} i\hbar = i, \qquad (2.5)$$

$$[\hat{a}, \hat{a}^{\dagger}] = \frac{1}{2} [(\hat{X} + i\hat{P}), \ (\hat{X} - i\hat{P})] = \frac{1}{2} \left(-i[\hat{X}, \hat{P}] + i[\hat{P}, \hat{X}] \right) = 1$$
(2.6)

The Hamiltonian can be expressed in these operators if we note from (2.4) that

$$\hat{X} = \frac{1}{\sqrt{2}}(\hat{a}^{\dagger} + \hat{a}) \text{ and } \hat{P} = \frac{i}{\sqrt{2}}(\hat{a}^{\dagger} - \hat{a})$$

This gives

$$\hat{H} = \frac{1}{2}\hbar\omega(\hat{P}^2 + \hat{X}^2) = \frac{\hbar\omega}{4} \left((\hat{a}^{\dagger} + \hat{a})^2 - (\hat{a}^{\dagger} - \hat{a})^2 \right) = \frac{\hbar\omega}{2} (\hat{a}^{\dagger}\hat{a} + \hat{a}\hat{a}^{\dagger})$$

= $\hbar\omega \left(\hat{a}^{\dagger}\hat{a} + \frac{1}{2} \right)$ (2.7)

If we introduce the operator $\hat{N} = \hat{a}^{\dagger}\hat{a}$ then $\hat{H} = \hbar\omega(\hat{N} + \frac{1}{2})$.

To get the energy spectrum we solve the eigenvalue problem for \hat{N} . Let $|\phi_n\rangle$ be an eigenstate and λ_n the corresponding eigenvalues so that $\hat{N}|\phi_n\rangle = \lambda_n |\phi_n\rangle$. We first note that the eigenvalues λ_n are non-negative:

$$\lambda_n = \langle \phi_n | \lambda_n | \phi_n \rangle = \langle \phi_n | \hat{a}^{\dagger} \hat{a} | \phi_n \rangle = \left[\langle \phi_n | \hat{a}^{\dagger} \right] \left[\hat{a} | \phi_n \rangle \right] = \langle \phi'_n | \phi'_n \rangle \ge 0.$$

where $|\phi'_n\rangle = \hat{a}|\phi_n\rangle$.

Secondly we will prove that the state $\hat{a}^{\dagger}|\phi_n\rangle$ is an eigenstate of \hat{N}

$$\hat{N}a^{\dagger}|\phi_{n}\rangle = \hat{a}^{\dagger}\hat{a}\hat{a}^{\dagger}|\phi_{n}\rangle = \hat{a}^{\dagger}(\hat{a}^{\dagger}\hat{a}+1)|\phi_{n}\rangle = \hat{a}^{\dagger}(\hat{N}+1)|\phi_{n}\rangle = (\lambda_{n}+1)\hat{a}^{\dagger}|\phi_{n}\rangle$$

(The expression $\hat{a}\hat{a}^{\dagger} = \hat{a}^{\dagger}\hat{a} + 1$ follows directly from (2.6)). By operating on eigenstates with \hat{a}^{\dagger} we get a new eigenstate with an eigenvalue that has been increased by 1. These kind of operators are called *step operators*. In the same way the operator \hat{a} decreases the eigenvalue by 1:

$$\hat{N}\hat{a}|\phi_n\rangle = (\lambda_n - 1)\hat{a}|\phi_n\rangle \tag{2.8}$$

The proof is left as an exercise. By using relation (2.8) k times we obtain

$$\hat{N}\hat{a}^{k}|\phi_{n}\rangle = (\lambda_{n} - k)\hat{a}^{k}|\phi_{n}\rangle$$
(2.9)

But all eigenvalues to \hat{N} are as we have seen non-negative. This means that it is not possible to continue forever generating new eigenstates by operating with \hat{a} . There must exist a state $|\phi_0\rangle$ such that $\hat{a}|\phi_0\rangle = 0$. Then $\hat{N}|\phi_0\rangle = \hat{a}^{\dagger}\hat{a}|\phi_0\rangle = 0$ which shows that $\lambda_0 = 0$ is the lowest eigenvalue and consequently $|\phi_0\rangle$ is the ground state of the Hamiltonian (2.7). Starting from this ground state it is easy to generate new eigenstates by using the step operator:

$$\hat{a}^{\dagger} |\phi_{0}\rangle = \alpha_{1} |\phi_{1}\rangle, \qquad \hat{N} \hat{a}^{\dagger} |\phi_{0}\rangle = \alpha_{1} |\phi_{1}\rangle, \\ (\hat{a}^{\dagger})^{2} |\phi_{0}\rangle = \alpha_{2} |\phi_{2}\rangle, \qquad \hat{N} (\hat{a}^{\dagger})^{2} |\phi_{0}\rangle = 2\alpha_{2} |\phi_{2}\rangle, \\ (\hat{a}^{\dagger})^{3} |\phi_{0}\rangle = \alpha_{3} |\phi_{3}\rangle, \qquad \hat{N} (\hat{a}^{\dagger})^{3} |\phi_{0}\rangle = 3\alpha_{3} |\phi_{3}\rangle, \dots$$

where α_n is a normalization constant and we see the eigenvalues of those states are $\lambda_n = n$.

For the one-dimensional harmonic oscillator, we will show in Sec. 2.2 using spatial representation that:

The set of eigenstates $\{|\phi_n\rangle\}_{n=0}^{\infty}$ is a complete set in the appropriate Hilbert space of the one-dimensional harmonic oscillator. This means that we have found all eigenstates and the eigenvalues are non-degenerate.

The eigenvalues of \hat{N} are all non-negative integers. This means that the energy eigenvalues for the Hamiltonian (2.1) are

$$E_n = \hbar \omega \left(n + \frac{1}{2} \right), \quad \text{for} \quad n = 0, 1, 2, \dots$$
 (2.10)

This is one of the standard spectra that every student of physics should know. In nature it is found mainly in vibrating systems such as molecules and nuclei.

Let us return to the final study of the step operators and the eigenstates. Because of the non-degeneracy the following relation holds $\hat{a}|\phi_n\rangle = c_n|\phi_{n-1}\rangle$, c_n =constant. This constant can be determined as follows

$$|c_n|^2 = \langle \phi_{n-1} | c_n^* c_n | \phi_{n-1} \rangle = \langle \phi_n | \hat{a}^{\dagger} \hat{a} | \phi_n \rangle = \langle \phi_n | n | \phi_n \rangle = n$$



Figure 2.1: Energy levels for a one dimensional harmonic oscillator. The arrows indicate the actions of the step operators

By custom one chooses the phase such that $c_n = \sqrt{n}$. Thus

$$\hat{a}|\phi_n\rangle = \sqrt{n}|\phi_{n-1}\rangle \tag{2.11}$$

In a similar manner one easily obtains

$$\hat{a}^{\dagger}|\phi_n\rangle = \sqrt{n+1}|\phi_{n+1}\rangle \tag{2.12}$$

These relations suggest the names *lowering* and *raising operators* for \hat{a} and \hat{a}^{\dagger} . By recursive use of (2.11) one can express all eigenstates as

$$|\phi_n\rangle = \frac{1}{\sqrt{n!}} (\hat{a}^{\dagger})^n |\phi_0\rangle \tag{2.13}$$

With this choice of phases, one frequently replaces $|\phi_n\rangle$ by the simplified notation $|n\rangle$. Note that $|0\rangle$ is here the ground state of the harmonic oscillator, which is a physical state with norm 1 and fundamentally different from $|null\rangle$, the only ket with norm 0.

The expressions (2.11) and (2.12) are very useful in calculating matrix elements as the following examples show.

Example: Calculate the matrix elements of \hat{a}^{\dagger} in the basis of $|n\rangle$.
2.1. ALGEBRAIC SOLUTION BY STEP OPERATORS

$$\langle m|\hat{a}^{\dagger}|n\rangle = \langle m|\sqrt{n+1}|n+1\rangle = \sqrt{n+1}\delta_{m,n+1}$$

When calculating matrix elements for \hat{x} or \hat{p} it is convenient to express these operators in step operators. From (2.2) and (2.4) one gets

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}} (\hat{a}^{\dagger} + \hat{a}), \quad \hat{p} = i\sqrt{\frac{m\hbar\omega}{2}} (\hat{a}^{\dagger} - \hat{a})$$
(2.14)

Example: Calculate the matrix elements of \hat{x}^2

Let us first express \hat{x}^2 in the step operators.

$$\frac{2m\omega}{\hbar}\hat{x}^2 = (\hat{a}^{\dagger} + \hat{a})^2 = (\hat{a}^{\dagger})^2 + \hat{a}^{\dagger}\hat{a} + \hat{a}\hat{a}^{\dagger} + \hat{a}^2$$

It is useful to use the commutation relation to rearrange this expression so that \hat{a}^{\dagger} precedes \hat{a} . We then get a *normal ordered product*.

$$(\hat{a}^{\dagger})^2 + \hat{a}^{\dagger}\hat{a} + \hat{a}\hat{a}^{\dagger} + \hat{a}^2 = (\hat{a}^{\dagger})^2 + \hat{a}^{\dagger}\hat{a} + \hat{a}^{\dagger}\hat{a} + 1 + \hat{a}^2 = (\hat{a}^{\dagger})^2 + 2\hat{a}^{\dagger}\hat{a} + \hat{a}^2 + 1$$

It is now easy to calculate the matrix elements:

$$\langle m | (\hat{a}^{\dagger})^{2} | n \rangle = \langle m | \hat{a}^{\dagger} \sqrt{n+1} | n+1 \rangle = \langle m | \sqrt{n+1} \sqrt{n+2} | n+2 \rangle$$

$$= \sqrt{(n+1)(n+2)} \delta_{m,n+2}$$

$$\langle m | \hat{a}^{\dagger} \hat{a} | n \rangle = \langle m | n | n \rangle = n \delta_{m,n}$$

$$\langle m | \hat{a}^{2} | n \rangle = \langle m | \hat{a}^{\dagger} \sqrt{n} | n-1 \rangle = \langle m | \sqrt{n} \sqrt{n-1} | n-2 \rangle$$

$$= \sqrt{n(n-1)} \delta_{m,n-2}$$

For a given n only the following matrix elements are non-disappearing:

$$\langle n+2|\hat{x}^2|n\rangle = \frac{\hbar}{2m\omega}\sqrt{(n+1)(n+2)}$$
$$\langle n|\hat{x}^2|n\rangle = \frac{\hbar}{2m\omega}(2n+1)$$
$$\langle n-2|\hat{x}^2|n\rangle = \frac{\hbar}{2m\omega}\sqrt{n(n-1)}$$

Note that matrix elements in the common spatial representations are defined as integrals and that we by this method have found a way to integrate a large class of them by algebraic methods. It is also interesting to note that we do not need to know any explicit formula for the eigenstate $|n\rangle$.

2.2 Eigenfunctions in spatial representation

We have so far not used any explicit representation of the eigenstates. Now the eigenstates shall be evaluated in spatial representation $\langle x | \phi_n \rangle = \phi_n(x)$, which are just the conventional wave-functions known from elementary courses. The idea is here to calculate the ground state wave-function $\phi_0(x)$ and then use the raising operator to generate the wave-function for the excited states. We start by expressing the step operators in spatial representation, where they become differential operators:

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i}{\sqrt{2m\hbar\omega}}\hat{p} \to \sqrt{\frac{m\omega}{2\hbar}}x + \sqrt{\frac{\hbar}{2m\omega}}\frac{\partial}{\partial x} = \frac{1}{\sqrt{2}}\left(\xi + \frac{\partial}{\partial\xi}\right)$$
(2.15)

where ξ is the spatial representation of the dimensionless operator \hat{X} introduced previously, i.e., $\xi = \sqrt{\frac{m\omega}{\hbar}}x$. In a similar manner one gets

$$\hat{a}^{\dagger} \to \frac{1}{\sqrt{2}} \left(\xi - \frac{\partial}{\partial \xi} \right)$$
 (2.16)

To get the ground state we solve the equation

$$\hat{a}|\phi_0\rangle = 0 \rightarrow \left(\xi + \frac{\partial}{\partial\xi}\right)\phi_0(\xi) = 0$$

which gives

$$\phi_0(\xi) = c_0 e^{-\frac{\xi^2}{2}}$$

The constant c_0 can be determined by normalization: $c_0 = \pi^{-1/4}$ Equation (2.13) gives us the expression for an arbitrary state:

$$\phi_n(\xi) = c_0 \frac{1}{\sqrt{2^n n!}} \left(\xi - \frac{d}{d\xi}\right)^n e^{-\frac{\xi^2}{2}}.$$
(2.17)

This could be rewritten to a more accessible form if we note that

$$\left(\xi - \frac{d}{d\xi}\right) \left(e^{\frac{\xi^2}{2}} u(\xi)\right) = \xi e^{\frac{\xi^2}{2}} u - \xi e^{\frac{\xi^2}{2}} u - e^{\frac{\xi^2}{2}} u' = \left(-e^{\frac{\xi^2}{2}} \frac{d}{d\xi}\right) u$$

Let us use this formula n times:

$$\left(\xi - \frac{d}{d\xi}\right)^n e^{-\frac{\xi^2}{2}} = \left(\xi - \frac{d}{d\xi}\right)^n e^{\frac{\xi^2}{2}} e^{-\xi^2} = (-1)^n e^{\frac{\xi^2}{2}} \frac{d^n}{d\xi^n} e^{-\xi^2}$$
(2.18)

The Hermite polynomials are defined by the relation

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2}$$
(2.19)

The first four are:

$$H_0(\xi) = 1 \qquad H_1(\xi) = 2\xi$$
$$H_2(\xi) = 4\xi^2 - 2 \qquad H_3(\xi) = 8\xi^3 - 12\xi$$

 $H_n(\xi)$ has parity $(-1)^n$ and degree *n*. An explicit expression for an arbitrary eigenstate is

$$\phi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \left(2^n n!\right)^{-1/2} H_n(\xi) e^{\frac{-\xi^2}{2}}, \quad \xi = \sqrt{\frac{m\omega}{\hbar}} x \quad (2.20)$$

(This state is normalized with respect to integration over x explaining the different prefactor.) We can now prove that we have indeed found all eigenstates and that the spectrum is non-degenerate. This follows from the fact that the Hermite polynomials form a complete set in the appropriate Hilbert space.

2.3 Two- and Three-Dimensional Harmonic Oscillator

In many applications harmonic oscillators with two or three dimensions are used. It is rather straight forward to extend the theory to higher dimensions. The Hamiltonian for a two dimensional oscillator is

$$\hat{H} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2) + \frac{1}{2}m\omega^2(\hat{x}^2 + \hat{y}^2) = \hbar\omega(\hat{a}_x^{\dagger}\hat{a}_x + \hat{a}_y^{\dagger}\hat{a}_y + 1)$$
(2.21)



Figure 2.2: Spectrum for a two dimensional harmonic oscillator. The degeneracy is marked in the level scheme.

with the step operators \hat{a}_x and \hat{a}_y

$$\hat{a}_x = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}_x, \quad \hat{a}_y = \sqrt{\frac{m\omega}{2\hbar}}\hat{y} + i\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}_y$$
(2.22)

Note that \hat{a}_x and \hat{a}_y commute. The eigenvalues to (2.21) are determined as in one dimensional case to be

$$E_{n_x n_y} = \hbar \omega (n_x + n_y + 1) \tag{2.23}$$

where n_x and n_y are non-negative integers. The corresponding eigenstates are in spatial representation

$$\phi_{n_x n_y}(x, y) = \phi_{n_x}(x)\phi_{n_y}(y) \tag{2.24}$$

These states are degenerate. To determine the degeneracy, we have to count the number of different ways that two non-negative integers can be added to give the result N. Thus $N = n_x + n_y$. n_x can be chosen in N + 1 different ways. But when n_y is determined to be $N - n_x$. The degeneracy is thus N + 1. This also follows directly from figure (2.2).

In three dimensions the Hamiltonian is

$$\hat{H} = \hbar\omega \left(\hat{a}_x^{\dagger} \hat{a}_x + \hat{a}_y^{\dagger} \hat{a}_y + \hat{a}_z^{\dagger} \hat{a}_z + \frac{3}{2} \right)$$
(2.25)



Figure 2.3: Spectrum for a three-dimensional harmonic oscillator with degeneracy.

with eigenvalues

$$E_{n_x n_y n_z} = \hbar \omega \left(n_x + n_y + n_z + \frac{3}{2} \right) \tag{2.26}$$

and eigenstates in spatial representation

$$\phi_{n_x n_y n_z}(x, y, z) = \phi_{n_x}(x)\phi_{n_y}(y)\phi_{n_z}(z)$$
(2.27)

It is a little trickier to determine the degeneracy in this case. In how many ways can three non-negative integers can be chosen when their sum is given? Denote $N = n_x + n_y + n_z$. If n_x is fixed then one can choose n_y and n_z in $n_y + n_z + 1 = N - n_x + 1$ different ways as was found in the two dimensional case. But for a given N, n_x can be picked in N + 1 different ways. The total number of possibilities is

$$\sum_{n_x=0}^{N} (N - n_x + 1) = \frac{(N+1) + 1}{2} (N+1) = \frac{1}{2} (N+2)(N+1).$$
(2.28)

In spatial representation the Hamiltonian becomes

$$\hat{H} \to -\frac{\hbar^2}{2m}\Delta + \frac{1}{2}m\omega^2(x^2 + y^2 + z^2) = -\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{L^2}{2mr^2} + \frac{1}{2}m\omega^2r^2 \quad (2.29)$$

where we have used spherical coordinates. The eigenstates to this spherical symmetric operator can be written as

$$\phi_{nlm}(r,\theta,\varphi) = \frac{u_{nl}(r)}{r} Y_l^m(\theta,\varphi)$$
(2.30)

For given quantum numbers n and l there is 2l+1 -fold degeneracy and the energy does not depend on m. The eigenvalue equation reduces to an ordinary differential equation:

$$-\frac{\hbar^2}{2m}u_{nl}'' + \left(\frac{\hbar^2 l(l+1)}{2mr^2} + \frac{1}{2}m\omega^2 r^2\right)u_{nl} = E_{nl}u_{nl}$$
(2.31)

We will not solve this equation here, but only give some results: The energy eigenvalues are, of course, the same as before but depend on the quantum numbers in a different way:

$$E_{n,l} = \hbar\omega \left(2n+l+\frac{3}{2}\right) \tag{2.32}$$

Obviously if N = 2n + l is even (odd) then also l is even(odd). If N = 0 the only values are: n = 0 and l = 0. The first excited state has N = 1. Then n = 0 and l = 1. In addition to this there are different *m*-values so that the degeneracy is 3 as we have already found. The eigenfunctions corresponding to this first excited state span a three dimensional subspace. There are as we have seen two natural bases in this subspace, corresponding to either Cartesian or spherical coordinates.

2.4 Harmonic Oscillator Model for Many-Particle Systems^{*}

2.4.1 Mean-field model and shell structure

So far, we have mainly been concerned with the single-particle properties of a quantum system, i.e. the eigenstates of a single particle trapped by a confinement potential. Many of the quantal systems occurring in nature, however, confine many particles, and it is the interaction between all these particles that determine the physical behavior of the quantum system as a whole. A famous example is the atom, with its nucleus being a many-particle system made from the nucleons, and its outer shell of many electrons, determining the structure of the periodic table.



Figure 2.4: Three dimensional harmonic oscillator in spherical coordinates. The figure shows the orbital quantum number and the degeneracy.

The quantum-mechanical description of such many-particle systems is a cumbersome task, and yet today, despite all the power of computation, large many-particle quantum systems can only be treated rather phenomenologically.

One of the simplest approximate models is based on the idea that the interactions, possibly together with an external confinement, create an average "mean field", which models the action of all the quantum particles on each other: Instead of individual particle-particle interactions, non-interacting particles are then assumed to move in a modified, effective confinement, that accounts for the interactions of all the particles with each other.

This a priori rather simple idea forms the basis of more complicated theories (some of which we will touch later on in these lecture notes).

The distribution of single-particle energy levels of the mean-field potential can be non-uniform and bunches of degenerate or nearly degenerate levels, being separated from other levels by energy gaps, can occur. Such groupings of levels are also called "shells", just like in atoms. They are schematically drawn in Fig. 2.5.

Shell structure is a consequence of both the dimensionality and of the symmetry

CHAPTER 2. THE HARMONIC OSCILLATOR



Figure 2.5: Schematic illustration of the bunching of single-particle states (shell structure) in a finite fermion system. The binding energy is lower, if the single-particle level density at the Fermi energy has a minimum (after Brack *et al.*, 1972).

of the mean field potential. A high degree of symmetry results in a pronounced level bunching $^{\rm 1}$

This level bunching is manifested in many of the physical properties of finite, quantal many-fermion systems, like, for example, in their stability, in the ionization energies, the chemical reactivity or in the conductance.

In the mean-field model in its very simplest form, the eigenstates of the meanfield potential (that models the confinement of the quantum particles together with their average interactions with each other) are filled with non-interacting fermions, respecting the Pauli principle. At zero temperature, the lowest states are filled up to a certain level, where one runs out of particles. This level is usually called the "Fermi level".

The density of single-particle states at the Fermi energy is of particular importance for the stability of the system. If it is at a minimum, the particles occupy states with a smaller energy on average, and consequently, the system is more bound:

¹see for example, Funny Hills: The Shell Correction Approach to Nuclear Shell Effects and its application to the fission process by M. M., J. Damgaard, A.S. Jensen, H.C. Pauli, V.M. Strutinsky, and C.Y. Wong, 1972, Rev. Mod. Phys. 44, 320.

shell filling leads to particularly stable states. Here, the nobel gases are very good examples. If a shell is not filled, however, the system can stabilize itself by spontaneously breaking its internal symmetry. For atomic nuclei, for example, such a spatial deformation of the mean field was confirmed by an analysis of rotational spectra²

More recently, similar effects were observed from plasmon resonances of metallic clusters.

In a finite quantal system of fermions, the stability condition is that there is no unresolved degeneracy at the Fermi energy. This condition is met for certain numbers of confined particles, for which a degenerate shell with a large energy gap to the next, unoccupied shell can be filled.

2.4.2 Shell structure of the 2D anisotropic harmonic oscillator

We illustrate this with the example of an anisotropic harmonic oscillator confinement in two dimensions (x, y),

$$V(x,y) = \frac{1}{2}m^*\omega_0^2 \left(\delta x^2 + \frac{1}{\delta}y^2\right),$$
(2.33)

as an empirical mean-field potential in which a number of N fermions with an effective mass m^* are assumed to move independently. The ratio $\delta = \omega_x/\omega_y$ with frequencies $\omega_x = \omega_0 \sqrt{\delta}$ and $\omega_y = \omega_0/\sqrt{\delta}$ defines the ratio of semi-axes of the ellipse equipotentials. Imposing the constraint $\omega_0^2 = \omega_x \omega_y$ conserves their area with deformation. The corresponding single-particle energy spectrum

$$\varepsilon_{n_x,n_y}(\delta) = \hbar\omega_0 \left[(n_x + \frac{1}{2})\sqrt{\delta} + (n_y + \frac{1}{2})/\sqrt{\delta} \right]$$
(2.34)

is shown as a function of deformation δ in Fig. 2.6 (left). In the isotropic case $\delta = 1$, one clearly recognizes the (N_0+1) -fold degeneracy for a principal quantum number $N_0 = n_x + n_y = 0, 1, 2, ...$ Filling the states with non-interacting fermions, respecting the Pauli principle and including spin degeneracy with a factor of two, closed shells can be reached for a sequence of N = 2, 6, 12, 20... particles.

 $^{^2 \}mathrm{see}$ the books on $Nuclear\ Structure$ by Å. Bohr and B. R. Mottelson, 1975



Figure 2.6: Left: Single-particle states of a two-dimensional anisotropic harmonic oscillator as a function of deformation ($\delta > 1$). Degeneracies in the isotropic case ($\delta = 1$) lead to closed shells for N = 2, 6, 12, 20, ... (for non-interacting fermions, including spin degeneracy) and subshells occur at frequency ratios $\delta =$ q/p for integer q, p. Right: Total energies $\sum_{n_x,n_y} \varepsilon_{n_x,n_y}$ of the anisotropic harmonic oscillator for N = 2, 4, 6, 8, 10, and 12 non-interacting particles as a function of deformation.

For these configurations, particular stability is reached, as the degeneracy of the shell is resolved and the density of states is minimal at the Fermi energy. Adding one more electron to a closed shell would result in single occupancy of an orbit belonging to the next, higher shell, and the system would be less stable. In the case of open shells, however, the degeneracy can be lowered by deformation and an energetically more favorable configuration can be reached.

In particular, for non-circular shapes, subshells with degeneracies comparable to the non-deformed case can occur, leading to a pronounced stability at the corresponding deformation.

Figure 2.6 (right) shows the total energies $\sum_{n_x,n_y} \varepsilon_{n_x,n_y}(\delta)$. We see that depending on the number of confined particles and deformation, cusps and minima in the total energy occur for $\delta > 1$ at frequency ratios where more pronounced subshells are formed. As it is already obvious from the shell patterns in the single-particle spectra, configurations with N = 2, 6, or 12 particles have lowest energies in the isotropic case, while for N = 4, 8 or 10, the energy can be lowered by deformation.

Despite the simplicity of this example, it already contains some of the basic features of a finite, fermionic quantum system: the occurrence of shells and the corresponding stability for closed-shell configurations, and the tendency to spontaneously break the symmetry of the mean field in the case of open shells. Subshell closings enhance the stability for the broken-symmetry states compared to the non-deformed, open-shell system.

2.4.3 "Magic numbers" in finite fermion systems

The periodic table with the appearance of its eight groups of elements showing similar chemical properties is the most widely appreciated example of shell structure. *Atomic shells* are most strikingly seen in the pronounced maxima of the ionization energies of neutral atoms for certain atomic numbers Z = 2, 10, 18..., corresponding to the noble gases He, Ne, Ar, ... (cf. upper left panel of Fig. 2.7).

The spherical symmetry of the very rigid confinement of the electrons caused by the strong Coulomb potential of the nucleus results in large degeneracies at the mid-shell regions. These shells are then populated according to Hund's rules: due to the Pauli principle and the repulsive Coulomb interaction, the spin is maximized for half-filled orbitals.

In *nuclei*, the separation energy (i.e. the energy that is required to remove a nucleon from the nucleus) of neutrons and protons shows sharp steps for certain particle numbers, originating from the shell structure (lower left panel of Fig. 2.7). These steps are very similar to the abrupt decrease of the atomic ionization potentials for electron numbers that exceed the atomic shell closings by one.

Parameterizing an average mean-field potential and including spin-orbit coupling, Goeppert-Mayer (1949) and Haxel, Jensen, and Suess (1949) could formulate a shell model that successfully explained the "magic numbers" of nucleons for which particular stability was observed.

In the early eighties finite-size *clusters of atoms* attracted much interest: they



Figure 2.7: Shell structure and "magic numbers" in finite fermion systems. Left, upper panel: Atomic ionization energies. Lower panel: Separation energies of atomic nuclei, after Bohr and Mottelson, 1975. Right, upper panel: Abundance spectra of metallic clusters (counting rate in arbitrary units) (after W.D. Knight, Clemenger, K., de Heer, W.A., Saunders, W.A., Chou, M.Y., and Cohen, M.L., 1984, Phys. Rev. Lett. **52**, 2141). Lower panel: Differences in the chemical potential $\mu(N + 1) - \mu(N)$ of disk-shaped quantum dots. Inset: Device setup, schematic (From Tarucha, S., D.G. Austing, T. Honda, R.J. van der Haage, and L. Kouwenhoven, 1996, Phys. Rev. Lett. **77**, 3613.)

2.4. HARMONIC OSCILLATOR MODEL FOR MANY-PARTICLE SYSTEMS*43

provided a link between the physics of single atoms or the smallest molecules, and the solid. Knight et al. (1984) succeeded to fabricate clusters consisting of a few up to hundreds of alkali atoms by supersonic expansion of a mixture of metal atoms and a carrier gas through a tiny nozzle. Condensation of droplets and subsequent evaporation of single atoms until equilibrium was reached, produced stable clusters which could then be counted and size-selected. The anomalies in the mass abundance spectra, i.e. the counting rates of clusters with a given number of atoms per cluster, are striking: for certain numbers of atoms, one observes an enhanced stability of the cluster. The upper right panel of Fig. 2.7 shows the cluster counting rate (in arbitrary units) as a function of the number of atoms per cluster: pronounced maxima are observed for clusters with 2, 8, 20, 40, and 58 atoms. This reminds us of the "magic numbers" in nuclei mentioned above. A metal cluster can be described in a simple model which assumes that the delocalized valence electrons experience a homogeneous positive charge background ("jellium") of the atom ions. This approach has long been used in solid state physics to describe, for example, metal surfaces, or voids in metals. Indeed, the jellium model of metals provided an explanation for the enhanced stability of clusters with specific sizes.

In beautiful analogy to atoms, nuclei, or clusters, shell structure can also be observed in the conductance spectra of small semiconductor quantum dots. As an example, the inset to Fig. 2.7 (lower right panel) schematically shows the device used by Tarucha et al. (1996): in an etched pillar of semiconducting material, a small, quasi two-dimensional electron island is formed between two heterostructure barriers. The island can be squeezed electrostatically by applying a voltage to the metallic side gate which is formed around the vertical structure. The dot is connected to macroscopic voltage and current meters via the source and drain contacts. Measuring the current as a function of the voltage on the gates at small source-drain voltage, one observes current peaks for each single electron subsequently entering the dot. The spacing between two subsequent current peaks is proportional to the difference in energy needed to add another electron to a dot already confining N particles. This quantity is plotted in Fig. 2.7 (lower right panel) for two different dots with diameters $D = 0.5 \ \mu m$ and $D = 0.44 \ \mu m$ and shows large amplitudes at electron numbers N = 2, 6, 12. Indeed, these numbers correspond to closed shells of a two-dimensional harmonic oscillator. As we shall discuss later in this course, the additional structures at the mid-shell regions are



Figure 2.8: A one dimensional model for lattice vibrations.

a consequence of the spin alignment due to Hund's rules, in much analogy to the atomic ionization spectra.

2.5 Phonons

As a last example of harmonic oscillators we will treat coupled oscillations of a chain of particles. This is a one-dimensional model for the real three dimensional crystal vibrations which play an important role in solid state physics. It is an important example also from a fundamental point of view, because we will here for the first time encounter *collective quantum states*. In these states there is a coherent motion of a large number of particles in contrast with the single particle states that have been studied up to now.

Consider a chain of N balls that are closed to a ring ("rosary"). Each ball has the same mass and between the balls there are identical harmonic springs. The distance between the balls in equilibrium is a and the spring constant is g.

As a first step we will study longitudinal classical waves on the rosary. Ball #l has the equilibrium position x = al. By u_l we denote the displacement from this point. The classical equation of motion follows from figure 2.9

The Newton equation of motion for ball #l is

$$m\frac{d^2u_l}{dt^2} = g\big((u_{l-1} - u_l) - (u_l - u_{l+1})\big) = g(u_{l-1} - 2u_l + u_{l+1})$$
(2.35)



Figure 2.9: Displacement along the rosary.

While the chain is closed we have periodic boundary conditions

$$u_{l+N} = u_l \,. \tag{2.36}$$

Motivated by a wave-type elongation $u(x,t) = Ae^{i(kx-\omega t)}$ for the discrete points $x_l = al$ we will now seek solutions to (2.35) in the form of

$$u_l(t) = A e^{i(kal - \omega t)}.$$
(2.37)

From the periodic boundary condition (2.36):

$$e^{i(kal-\omega t)} = e^{i(k(a(l+N))-\omega t)} \Rightarrow e^{ikNa} = 1 \Rightarrow kNa = 2\pi r' \text{ with } r' \in \mathbb{Z}$$

Now k values, which differ by multiples of $2\pi/a$ provide identical elongations for all lattice sites in Eq. (2.37). Thus one can restrict to $-\pi/a < k \leq \pi/a$ (which is actually called the first Brillouin zone for crystals). Assuming in the following an even number N of balls, the corresponding k values, which describe the different collective waves off the chain, can be numbered in the form

$$k_r = \frac{2\pi}{Na} \left(r - \frac{N}{2} \right) \quad \text{with} \quad r = 1, 2, \dots N \tag{2.38}$$

Note that the number of different collective waves (or modes) equals the number of balls on the chain. Using the ansatz(2.37) in the equation of motion we get

$$-m\omega^2 e^{i(kla-\omega t)} = gAe^{i(k(l-1)a-\omega t)} - 2e^{i(kla-\omega t)} + e^{i(k(l+1)a-\omega t)}.$$
 (2.39)

Some trivial algebra gives $\omega^2 = \frac{2g}{m}(1 - \cos(ka)) = \frac{4g}{m}\sin^2\left(\frac{ka}{2}\right)$. The dispersion relation is then given by

$$\omega(k) = 2\sqrt{\frac{g}{m}} \left| \sin\left(\frac{ka}{2}\right) \right| \,. \tag{2.40}$$



Figure 2.10: The dispersion relation for a harmonic wave along the rosary.

This function is plotted in Fig. 2.10

Let us now turn to the quantum mechanical problem. The Hamiltonian is in this case the sum of kinetic and potential energy. The potential energy is stored in the stressed springs. One gets

$$\hat{H} = \frac{1}{2m} \sum \hat{p}_l^2 + \frac{g}{2} \sum (\hat{u}_l - \hat{u}_{l-1})^2.$$
(2.41)

Here \hat{u}_l and \hat{p}_l are quantum mechanical operators that satisfies the usual commutation relations between position and momentum operators: $[\hat{u}_l, \hat{p}_l] = i\hbar$. In the case of several particles we generalize

$$[\hat{u}_l, \hat{p}_{l'}] = i\hbar\delta_{ll'} \tag{2.42}$$

When the classical wave (2.37) propagates through the lattice all balls move at the same time with the same amplitude but with different phases. We define collective operators as follows.

$$\hat{U}_k = \frac{1}{\sqrt{N}} \sum_{l=0}^{N-1} e^{ikla} \hat{u}_l, \qquad \hat{P}_k = \frac{1}{\sqrt{N}} \sum_{l=0}^{N-1} e^{-ikla} \hat{p}_l$$
(2.43)

We shall soon see that the Hamiltonian becomes simpler if we change to these operators. Note that these operators are non-Hermitian. It is obvious that $\hat{U}_k^{\dagger} = \hat{U}_{-k}$, $\hat{P}_k^{\dagger} = \hat{P}_{-k}$

2.5. PHONONS

The commutator between these operators is

$$\begin{aligned} [\hat{U}_{k}, \hat{P}_{k'}] &= \frac{1}{N} \sum_{ll'} e^{i(kl-k'l')a} [\hat{u}_{l}, \hat{p}_{l'}] = \frac{i\hbar}{N} \sum_{ll'} e^{i(kl-k'l')a} \delta_{ll'} \\ &= \frac{i\hbar}{N} \sum_{l} e^{i(k-k')la} = i\hbar \delta_{kk'} \end{aligned}$$
(2.44)

We have summed a geometrical series to obtain

$$\sum_{l=0}^{N-1} e^{i(k-k')la} = \sum_{l=0}^{N-1} (e^{i(k-k')a})^l = \frac{1-e^{i(k-k')Na}}{1-e^{i(k-k')a}} = \begin{cases} 0 & k \neq k' \\ N & k = k' \end{cases}$$
(2.45)

for the k-values satisfying Eq. (2.38). The relations (2.43) are some kind of discrete Fourier transform. These transforms can be inverted in the usual manner.

$$\hat{u}_l = \frac{1}{\sqrt{N}} \sum_k e^{-ikla} \hat{U}_k , \quad \hat{p}_l = \frac{1}{\sqrt{N}} \sum_k e^{ikla} \hat{P}_k$$
(2.46)

We can rewrite the Hamiltonian (2.41) with these expressions. A small technical difficulty comes from the fact that the operators defined by (2.43) are non-Hermitian. A simple way out is to rewrite the Hamiltonian in an explicit Hermitian way

$$\hat{H} = \frac{1}{2m} \sum \hat{p}_l^{\dagger} \hat{p}_l + \frac{g}{2} \sum (\hat{u}_l^{\dagger} - \hat{u}_{l-1}^{\dagger}) (\hat{u}_l - \hat{u}_{l-1}) .$$
(2.47)

Using (2.46) we can after some algebra write (2.47) as

$$\hat{H} = \sum_{k} \left(\frac{1}{2m} \hat{P}_{k}^{\dagger} \hat{P}_{k} + \frac{1}{2} m \omega^{2}(k) \hat{U}_{k}^{\dagger} \hat{U}_{k} \right).$$
(2.48)

The dispersion relation $\omega(k)$ is the same as the classical case given by (2.40). The Hamiltonian is the sum of independent, one dimensional harmonic oscillators. As for ordinary operators we can for each k-value define the step operators

$$\hat{a}_{k} = \sqrt{\frac{m\omega(k)}{2\hbar}} \hat{U}_{k} + i \frac{1}{\sqrt{2m\hbar\omega(k)}}} \hat{P}_{k}^{\dagger}$$

$$\hat{a}_{k}^{\dagger} = \sqrt{\frac{m\omega(k)}{2\hbar}} \hat{U}_{k}^{\dagger} - i \frac{1}{\sqrt{2m\hbar\omega(k)}}} \hat{P}_{k}$$
(2.49)

It is left as an exercise to prove the commutation relations

$$[\hat{a}_k, \hat{a}_{k'}^{\dagger}] = \delta_{kk'}, \quad [\hat{a}_k, \hat{a}_{k'}] = 0, \text{ and } \quad [\hat{a}_k^{\dagger}, \hat{a}_{k'}^{\dagger}] = 0$$
 (2.50)

All other commutators are zero. The Hamiltonian can be expressed in step operators as

$$\hat{H} = \sum_{k} \hbar \omega(k) \left(\hat{a}_{k}^{\dagger} \hat{a}_{k} + \frac{1}{2} \right)$$
(2.51)

As for ordinary one-dimensional step operators the commutation relation (2.50) results in the eigenvalue relation

$$\hat{a}_{k}^{\dagger}\hat{a}_{k}|\phi_{n}^{(k)}\rangle = n_{k}|\phi_{n}^{(k)}\rangle$$
 for $n_{k} = 0, 1, 2, \dots$ (2.52)

for each mode k. Now we apply the numbering from Eq. (2.38) and use the natural numbers r = 1, 2, ..., N to describe the different k-modes. Then each mode is in a certain state n_r and the total energy for the Hamiltonian (2.51) is just given by

$$E_{n_1,n_2,\dots} = \sum_r \hbar\omega(k_r) \left(n_r + \frac{1}{2}\right).$$
(2.53)

The eigenvalue problem is now formally solved. The corresponding eigenstates can be constructed from the ground state, corresponding to the quantum numbers $n_1 = n_2 = ... = 0$ which is just $|0, 0, ...\rangle$ and is defined by

$$\hat{a}_{k_r}|0,0,\ldots\rangle = 0$$
 for all r . (2.54)

By applying the step operator $\hat{a}^{\dagger}_{k_r}$ one obtains

$$\hat{a}_{k_r}^{\dagger}|0,0,\ldots\rangle = |0,0,\ldots,n_r = 1,0,\ldots\rangle$$
 (2.55)

The energy of this new state is $\hbar\omega(k_r)$ above the ground state energy. The quantum state $|0, 0, ..., n_r = 1, 0, ...\rangle$ corresponds to a classical wave with wavenumber k_r . Such a quantized wave carries both momentum and energy and is in many respects similar to a photon and is called a *phonon*. The energy of the phonon is $\hbar\omega(k_r)$ in close analogy with the photon case. The operator $\hat{a}_{k_r}^{\dagger}$ is naturally called *phonon* creation operator.

Repeating this operation, we obtain the general state as

$$|n_1, n_2, \dots n_N\rangle = \left[\prod_{r=1}^N \frac{1}{\sqrt{n_r!}} \left(\hat{a}_{k_r}^{\dagger}\right)^{n_r}\right] |0, 0, \dots\rangle$$
 (2.56)

2.5. PHONONS

The ground state $|0, 0, ...\rangle$ is called the *phonon vacuum*. It is customary to redefine the energy so that this state has the energy 0. To do this one subtracts a constant sum from the Hamiltonian³ and gets

$$\hat{H} = \sum_{r} \hbar \omega(k_r) \hat{a}_{k_r}^{\dagger} \hat{a}_{k_r} , \quad E_{n_1, n_2, \dots} = \sum_{r} \hbar \omega(k_r) n_{k_r}.$$
(2.57)

Example: Show that $|0, 0, \ldots n_r = 2, 0, \ldots\rangle$ defined by Eq. (2.56) is indeed an eigenstate of \hat{H} as in Eq. (2.57)

We have

$$|0, 0, \dots n_r = 2, 0, \dots \rangle = \frac{1}{\sqrt{2}} (\hat{a}_{k_r}^{\dagger})^2 |0, 0, \dots \rangle$$

Now we consider

$$\hat{H}|0,0,\dots n_r = 2,0,\dots\rangle = \frac{1}{\sqrt{2}} \sum_{r'} \hbar \omega(k_{r'}) \hat{a}^{\dagger}_{k_{r'}} \hat{a}_{k_{r'}} (\hat{a}^{\dagger}_{k_r})^2 |0,0,\dots\rangle$$

For $r' \neq r$ the commutation relation (2.50) provide $\hat{a}_{k_{r'}}(\hat{a}_{k_r}^{\dagger})^2 = (\hat{a}_{k_r}^{\dagger})^2 \hat{a}_{k_{r'}}$ and thus we can use the fact that $\hat{a}_{k_{r'}}|0,0,\ldots\rangle = 0$ to show that these terms do not provide any contribution. Thus only the term r' = r of the sum survives. Now the commutation relations (2.50) provide

$$\hat{a}_{k_r}\hat{a}_{k_r}^{\dagger}\hat{a}_{k_r}^{\dagger} = (\hat{a}_{k_r}^{\dagger}\hat{a}_{k_r} + 1)\hat{a}_{k_r}^{\dagger} = \hat{a}_{k_r}^{\dagger}(\hat{a}_{k_r}^{\dagger}\hat{a}_{k_r} + 1) + \hat{a}_{k_r}^{\dagger} = \hat{a}_{k_r}^{\dagger}\hat{a}_{k_r}^{\dagger}\hat{a}_{k_r} + 2\hat{a}_{k_r}^{\dagger}$$

Thus we find

$$\hat{H}|0,0,\ldots,n_r = 2,0,\ldots\rangle = \frac{1}{\sqrt{2}}\hbar\omega(k_r)2(\hat{a}_{k_r}^{\dagger})^2|0,0,\ldots\rangle$$
$$= 2\hbar\omega(k_r)|0,0,\ldots,n_r = 2,0,\ldots\rangle$$

and the state is indeed an eigenstate with the correct energy.

³While the ground state energy is neglected in many cases, it actually can play a role, if the frequency of the phonon modes changes by an external parameter (such as, e.g. a change of the coupling g following the geometry of the chain), which changes the total energy of the ground state. This corresponds to an effective force on the system. The same effects appears in the quantisation of the electromagnetic field, where this force is called Casimir force. It has some relevance in microstuctured geometries, see A.W. Rodriguez, F. Capasso, and S.G. Johnson, Nature Photonics, **5**, 211 (2011)

In a similar way this can be shown for arbitrary phonon states. This shows that phonons can be created one after each other independently of each other, which means that they do not interact with each other. Furthermore there can be arbitrarily many phonons in each state. (This is entirely different from the filling of electronic states, where the Pauli principle forbids multiple occupancy.) With the help of creation and annihilation operators all other operators representing physical entities can be constructed. We thus have a complete mathematical model to describe the physics of lattice vibrations. In order to use it in solid state physics we must consider vibrations in three-dimensional structures in transverse and longitudinal modes.

2.6 Coherent states*

The energy eigenstates $|n\rangle$ provide the expectation values

$$\langle n|\hat{x}|n\rangle = 0$$
 and $\langle n|\hat{p}|n\rangle = 0$

Thus they do not resemble a classical oscillation, where x and p oscillate in time. However there are states $|\Psi(t)\rangle$ which resemble the classical picture in a much better way. A very interesting class of such states are the coherent (or Glauber) states

$$|\alpha\rangle = \sum_{n} e^{-|\alpha|^2/2} \frac{\alpha^n}{\sqrt{n!}} |n\rangle$$
 for arbitrary complex α (2.58)

These states are actually eigenstates of the lowering operator

$$\hat{a}|\alpha\rangle = \sum_{n} e^{-|\alpha|^2/2} \frac{\alpha^n}{\sqrt{n!}} \sqrt{n} |n-1\rangle = \alpha \sum_{n} e^{-|\alpha|^2/2} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} |n-1\rangle = \alpha |\alpha\rangle \quad (2.59)$$

with eigenvalue α . (Note that \hat{a} is not Hermitean. Thus, eigenstates to different eigenvalues α are neither orthogonal, nor do they satisfy the closure relation.) As the coherent states are not eigenstates of the Hamiltonian, they have a more

complicated time dependence. For the initial condition $|\Psi(t=0)\rangle = |\alpha_0\rangle$ we find

$$|\Psi(t)\rangle = \sum_{n} e^{-|\alpha_{0}|^{2}/2} \frac{\alpha_{0}^{n}}{\sqrt{n!}} e^{-i\left(n+\frac{1}{2}\right)\omega t} |n\rangle = e^{-i\omega t/2} \sum_{n} e^{-\left|\alpha_{0}e^{-i\omega t}\right|^{2}/2} \frac{\left(\alpha_{0}e^{-i\omega t}\right)^{n}}{\sqrt{n!}} |n\rangle$$
$$= e^{-i\omega t/2} |\alpha(t)\rangle \quad \text{with } \alpha(t) = \alpha_{0} e^{-i\omega t}$$
(2.60)

Thus an initial coherent states is also a coherent states for later time with a change in the phase of α (as well as a multiplicative phase $e^{-i\omega t/2}$, which is not of relevance for any observable).

In order to calculate the expectation values of space and momentum we use Eq. (2.14) and $\langle \alpha | \hat{a}^{\dagger} = \alpha^* \langle \alpha |$. Then we find

$$\langle \alpha | \hat{x} | \alpha \rangle = \sqrt{\frac{\hbar}{2m\omega}} (\alpha^* + \alpha) = \sqrt{\frac{2\hbar}{m\omega}} \operatorname{Re} \{\alpha\}$$
 (2.61)

$$\langle \alpha | \hat{p} | \alpha \rangle = i \sqrt{\frac{\hbar m \omega}{2}} (\alpha^* - \alpha) = \sqrt{2\hbar m \omega} \operatorname{Im} \{\alpha\}$$
 (2.62)

With the time dependence $\alpha(t) = \alpha_0 e^{-i\omega t}$, the averages reproduce the classical trajectories in phase space, as can be seen in Fig. 2.11.

In the same spirit (and using $\hat{a}\hat{a}^{\dagger} = \hat{a}^{\dagger}\hat{a} + 1$) we obtain

$$\langle \alpha | \hat{x}^2 | \alpha \rangle = \frac{2\hbar}{m\omega} (\operatorname{Re} \{\alpha\})^2 + \frac{\hbar}{2m\omega}$$
 (2.63)

$$\langle \alpha | \hat{p}^2 | \alpha \rangle = 2\hbar m \omega (\text{Im} \{\alpha\})^2 + \frac{\hbar m \omega}{2}$$
 (2.64)

This provides the variance

$$\Delta x = \sqrt{\langle \alpha | \hat{x}^2 | \alpha \rangle - \langle \alpha | \hat{x} | \alpha \rangle^2} = \sqrt{\frac{\hbar}{2m\omega}}$$
(2.65)

$$\Delta p = \sqrt{\langle \alpha | \hat{p}^2 | \alpha \rangle - \langle \alpha | \hat{p} | \alpha \rangle^2} = \sqrt{\frac{\hbar m \omega}{2}}$$
(2.66)

which describe the scattering of measurement results around the expectation value as indicated in Fig.2.11. We find that Δx is just the maximal elongation divided by $2|\alpha|$. Thus the relative fluctuations in the measurement results for the position vanish in the limit of larger $|\alpha|$. The same holds for Δp , so that we recover



Figure 2.11: Motion of a Glauber state with $\alpha_0 = 3$. The red circle is the classical trajectory, which is identical to the expectation values for space and momentum. The magenta area denotes the range of typical measurement values for x and p at a given time. (Note that only one of them can be measured for each preparation of the system.)

the classical behavior with well defined position and momentum for $|\alpha| \to \infty$. Furthermore we find the product

$$\Delta x \Delta p = \frac{\hbar}{2} \tag{2.67}$$

which is the lowest possible value according to the Heisenberg uncertainty relation.

Chapter 3

Angular momentum

3.1 Orbital Angular Momentum and Rotations

Following the classical expression, the operator of (orbital) angular momentum is $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$. The canonical commutation relations between $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ provide

$$[\hat{L}_j, \hat{L}_k] = i\hbar \sum_l \epsilon_{jkl} \hat{L}_l \tag{3.1}$$

where ϵ_{jkl} is the Levi-Civita symbol.¹ Now we shall relate these to rotations in the three dimensional space.

3.1.1 Rotations

A rotation \hat{U}_R transforms an arbitrary quantum state $|\Psi\rangle$ into the rotated state $|\Psi'\rangle$. Now we consider this rotation for quantum states in spatial representation, i.e. wave functions $\Psi(\mathbf{r})$. The same operation can be performed to the spatial vectors in the form $\mathbf{r}' = \mathcal{R}\mathbf{r}$. Consider for a certain point \mathbf{r}_0 in space the value the rotated wave function $\Psi'(\mathbf{r}) = \hat{U}_R^{\mathrm{SR}}\Psi(\mathbf{r})$ at the rotated position $\mathbf{r}'_0 = \mathcal{R}\mathbf{r}_0$. Obviously, this value is equal to the original wave function at the original position, i.e., $\Psi'(\mathbf{r}'_0) = \Psi(\mathbf{r}_0)$ holds. Now we set $\mathbf{r}_1 = \mathbf{r}'_0$ and find $\mathcal{R}^{-1}\mathbf{r}_1 = \mathbf{r}_0$. Thus we

 $^{{}^{1}\}epsilon_{jkl} = 0$ if two or three of the indices are equal. Otherwise $\epsilon_{123} = \epsilon_{231} = \epsilon_{312} = 1$ (cyclic permutation of 123) and $\epsilon_{132} = \epsilon_{213} = \epsilon_{321} = -1$.

Figure 3.1: We consider a rotation \mathcal{R} of $\pi/4$ (45°) around the origin. The spatial vector \mathbf{r} is mapped accordingly to \mathbf{r}' and the wave function $\Psi(\mathbf{r})$ to $\Psi'(\mathbf{r})$. We see that $\Psi'(\mathbf{r})$ is the same as $\Psi(\mathcal{R}^{-1}\mathbf{r})$, where the argument is rotated backwards ($\varphi \rightarrow \varphi - \pi/4$).



identify $\Psi'(\mathbf{r}_1) = \Psi(\mathcal{R}^{-1}\mathbf{r}_1)$. Now any point in space \mathbf{r} can be identified with \mathbf{r}_1 by constructing an appropriate $\mathbf{r}_0 = \mathcal{R}^{-1}\mathbf{r}$, so that we have the general identity

$$\hat{U}_R^{\mathrm{SR}}\Psi(\mathbf{r}) = \Psi'(\mathbf{r}) = \Psi(\mathcal{R}^{-1}\mathbf{r})$$

which is schetched in Fig. 3.1. In particular we consider an infinitesimal rotation with angle $\delta \phi$, where the direction of the vector denotes the axis of rotation. We find $\mathcal{R}\mathbf{r} = \mathbf{r} + \delta \phi \times \mathbf{r}$ and

$$\begin{split} \Psi'(\mathbf{r}) &= \Psi(\mathbf{r} - \delta \boldsymbol{\phi} \times \mathbf{r}) \approx \Psi(\mathbf{r}) - (\delta \boldsymbol{\phi} \times \mathbf{r}) \cdot \nabla \Psi(\mathbf{r}) \\ &= \Psi(\mathbf{r}) - \frac{\mathrm{i}}{\hbar} \delta \boldsymbol{\phi} \cdot \left(\mathbf{r} \times \frac{\hbar}{\mathrm{i}} \nabla \right) \Psi(\mathbf{r}) = \left(1 - \frac{\mathrm{i}}{\hbar} \delta \boldsymbol{\phi} \cdot \hat{\mathbf{L}}^{\mathrm{SR}} \right) \Psi(\mathbf{r}) \end{split}$$

where $\hat{\mathbf{L}}^{\text{SR}}$ is just the spatial representation of $\hat{\mathbf{L}}$. In the second line we used the fact, that ∇ can be treated as a vector, and the cyclic properties of the triple product.

The spatial representation of the orbital angular momentum $\hat{\mathbf{L}}^{SR} = \mathbf{r} \times \frac{\hbar}{i} \nabla$ generates infinitesimal rotations of wavefunctions in the three-dimensional space.

For a finite angle ϕ , we can integrate the infinitesimal relation and find

$$\Psi'(\mathbf{r}) = e^{-i\boldsymbol{\phi}\cdot\hat{\mathbf{L}}^{SR}/\hbar}\Psi(\mathbf{r})$$

so that the rotation by an angle ϕ is given by the operator

$$\hat{U}_{\phi} = e^{-i\phi \cdot \hat{\mathbf{L}}/\hbar} = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i\phi \cdot \hat{\mathbf{L}}}{\hbar}\right)^n$$
(3.2)

Note that \hat{U}_{ϕ} is unitary because $\hat{\mathbf{L}}$ is Hermitian.

Now we want to relate the commutations relations (3.1) to the properties of rotations in space. Here we treat $[\hat{L}_x, \hat{L}_y]$ explicitly, the others are fully analogous.

Consider two rotations around the x and y axis by (small) angles ϕ_x and ϕ_y , which we call \hat{U}_x and \hat{U}_y , respectively. They can be performed in two different sequences as $\hat{U}_x \hat{U}_y$ or $\hat{U}_y \hat{U}_x$. If the sequence does not play a role the product $(\hat{U}_y \hat{U}_x)^{-1} \hat{U}_x \hat{U}_y = \hat{U}_x^{\text{SR}-1} \hat{U}_y^{\text{SR}-1} \hat{U}_x \hat{U}_y$ should be the unit operator. (Note here that $(\hat{A}\hat{B})^{-1} = \hat{B}^{-1} \hat{A}^{-1}$ holds generally for linear operators.) We calculate this up to order ϕ^2 and find:

$$\begin{split} \hat{U}_{x}^{-1} \hat{U}_{y}^{-1} \hat{U}_{x} \hat{U}_{y} &= \left(1 + \frac{\mathrm{i}\phi_{x} \hat{L}_{x}}{\hbar} - \frac{(\phi_{x} \hat{L}_{x})^{2}}{2\hbar^{2}} \right) \left(1 + \frac{\mathrm{i}\phi_{y} \hat{L}_{y}}{\hbar} - \frac{(\phi_{y} \hat{L}_{y})^{2}}{2\hbar^{2}} \right) \\ &\times \left(1 - \frac{\mathrm{i}\phi_{x} \hat{L}_{x}}{\hbar} - \frac{(\phi_{x} \hat{L}_{x})^{2}}{2\hbar^{2}} \right) \left(1 - \frac{\mathrm{i}\phi_{y} \hat{L}_{y}}{\hbar} - \frac{(\phi_{y} \hat{L}_{y})^{2}}{2\hbar^{2}} \right) + \mathcal{O}\{\phi^{3}\} \\ &= 1 + \frac{\phi_{x} \phi_{y}}{\hbar^{2}} \left(-\hat{L}_{x} \hat{L}_{y} + \hat{L}_{y} \hat{L}_{x} \right) + \mathcal{O}\{\phi^{3}\} \\ &= 1 - \frac{\mathrm{i}}{\hbar} \phi_{x} \phi_{y} \hat{L}_{z} + \mathcal{O}\{\phi^{3}\} \end{split}$$

Thus the commutator relation $[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$ implies that a rotation around the z axis by the angle $\phi_x \phi_y$ remains, and the order in which rotations around different axis are performed is not arbitrary.

Exercise: Try this by rotating a box subsequently by 90° in *y*-direction, by 90° in *x*-direction, by -90° in *y*-direction, and by -90° in *x*-direction. What do you find? (You need much smaller angles in order to find a pure *z* rotation as a result.)

The fact that the commutator between \hat{L}_x and \hat{L}_y is finite, relates to the geometrical observation, that rotations around the x and y axis do not commute.

3.1.2 Spectrum and eigenstates

In spatial representation the operators of the orbital angular momentum can be easily expressed in spherical coordinates (r, θ, φ) as

$$\hat{L}_{z}^{\mathrm{SR}} = \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial \varphi} \qquad (\hat{\mathbf{L}}^{\mathrm{SR}})^{2} = -\hbar^{2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^{2} \theta} \frac{\partial^{2}}{\partial \varphi^{2}} \right]$$

Thus eigenstates of $\hat{L}_z^{\rm SR}$ satisfy

$$\hat{L}_z^{\rm SR}\Psi(r,\theta,\varphi) = m\hbar\Psi(r,\theta,\varphi) \quad \Rightarrow \Psi(r,\theta,\varphi) \propto e^{\mathrm{i}m\varphi}$$

As $\Psi(r, \theta, \varphi + 2\pi) = \Psi(r, \theta, \varphi)$ holds in the three dimensional space, we obtain the condition that $m \in \mathbb{Z}$. Thus the operator $(\hat{\mathbf{L}}^{\mathrm{SR}})^2$ can only have the eigenvalues $l(l+1)\hbar^2$ with $l \in \mathbb{N}_0$, where j is replaced by l as common for orbital angular momentum.

The common eigenfunctions of $(\hat{\mathbf{L}}^{SR})^2$ and \hat{L}_z^{SR} are the *spherical harmonics* $Y_l^m(\theta,\varphi)$ with the properties

$$(\hat{\mathbf{L}}^{\mathrm{SR}})^2 Y_l^m(\theta,\varphi) = l(l+1)\hbar^2 Y_l^m(\theta,\varphi) \quad \text{for} \quad l = 0, 1, 2, \dots$$
$$\hat{L}_z^{\mathrm{SR}} Y_l^m(\theta,\varphi) = m\hbar Y_l^m(\theta,\varphi) \quad \text{for} \quad m = -l, -l+1, \dots l$$

For further reference:

The spherical harmonics $Y_l^m(\theta, \varphi)$ satisfy the orthogonality

$$\int_{-1}^{1} d\cos\theta \, \int_{0}^{2\pi} d\varphi \left[Y_{l'}^{m'}(\theta,\varphi) \right]^* Y_{l}^{m}(\theta,\varphi) = \delta_{l',l} \delta_{m',m}$$

and read:

$$Y_l^m(\theta,\varphi) = (-1)^{(m+|m|)/2} \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} P_l^{|m|}(\cos\theta) e^{\mathrm{i}m\varphi}$$

with the Legendre polynomials $P_l^m(x)$ defined by

$$P_l^0(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l \qquad \text{for} \quad l = 0, 1, 2, \dots$$
$$P_l^m(x) = (1 - x^2)^{m/2} \frac{d^m}{dx^m} P_l^0(x) \qquad \text{for} \quad m = 0, 1, 2, \dots l$$

see, e.g., Arfken and Weber Mathematical Methods for Physicists². In particular

$$Y_0^0(\theta,\varphi) = \sqrt{\frac{1}{4\pi}} \qquad Y_1^0(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\theta$$
$$Y_1^1(\theta,\varphi) = -\sqrt{\frac{3}{8\pi}}\sin\theta \,e^{\mathrm{i}\varphi} \qquad Y_1^{-1}(\theta,\varphi) = \sqrt{\frac{3}{8\pi}}\sin\theta \,e^{-\mathrm{i}\varphi}$$

We find $Y_l^m(\pi - \theta, \varphi + \pi) = (-1)^l Y_l^m(\theta, \varphi)$, thus the spherical harmonics are eigenstates of the inversion $\mathbf{r} \to -\mathbf{r}$ with eigenvalue $(-1)^l$.

²Abramowitz and Stegun Handbook of Mathematical functions includes a factor $(-1)^m$ for $P_l^m(x)$.

3.2 Algebra of Angular Momentum

The commutation relations of the angular momentum have their origin in the transformations of objects under rotations. In an arbitrary ket space, we consider an infinitesimal rotation around the x-axis with angle $\delta\phi$. Then, any ket $|a\rangle$ is mapped onto another ket $|a'\rangle$ via a linear operator \hat{U}_x . As the norm of any ket is conserved under rotations, \hat{U}_x needs to be unitary. For small angles the changes in the state are proportional to $\delta\phi$ and we can write

$$\hat{U}_x = 1 - \frac{\mathrm{i}\delta\phi}{\hbar}\hat{J}_x$$
 with an Hermitian operator \hat{J}_x

This generator of rotations around the x-axis, \hat{J}_x , is referred to as a general *angular* momentum operator and the corresponding operators \hat{J}_y and \hat{J}_z are analogously defined. Based on the geometrical rules, how rotations around different axis commute, we find

In an arbitrary ket space the Hermitian angular momentum operators $\hat{J}_x, \hat{J}_x, \hat{J}_y$ satisfy

$$[\hat{J}_j, \hat{J}_k] = i\hbar \sum_l \epsilon_{jkl} \hat{J}_l$$
(3.3)

This is the algebra of angular momentum.

Based on the <u>algebra</u> and the fact that \hat{J} is <u>Hermitian</u> we can deduce all the other properties discussed in the rest of this chapter.

We define the square of the angular momentum $\hat{\mathbf{J}}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$ satisfying $[\hat{\mathbf{J}}^2, \hat{J}_j] = 0$ and the shift operators $\hat{J}_{\pm} = \hat{J}_x \pm i\hat{J}_y$ satisfying $(\hat{J}_{\pm})^{\dagger} = \hat{J}_{\mp}$

Proof of: $[\hat{J}^2, \hat{J}_j] = 0$:

Let j = z (for the other components, the proof works similarly). Then we have

$$\begin{split} [\hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2, \hat{J}_z] = & [\hat{J}_x^2, J_z] + [\hat{J}_y^2, \hat{J}_z] \\ = & \hat{J}_x \underbrace{[\hat{J}_x, \hat{J}_z]}_{=-\mathrm{i}\hat{J}_y} + \underbrace{[\hat{J}_x, \hat{J}_z]}_{=-\mathrm{i}\hat{J}_y} \hat{J}_x + \hat{J}_y \underbrace{[\hat{J}_y, \hat{J}_z]}_{=\mathrm{i}\hat{J}_x} + \underbrace{[\hat{J}_y, \hat{J}_z]}_{=\mathrm{i}\hat{J}_x} \hat{J}_y = 0 \end{split}$$

3.2.1 Determining the eigenvalues

As $[\hat{\mathbf{J}}^2, \hat{J}_z] = 0$, there exists a basis of an appropriate ket space consisting of common eigenstates of the operators $\hat{\mathbf{J}}^2$ and \hat{J}_z . Let $|\Psi\rangle$ be such a normalized state. In the following we will determine the properties of the corresponding eigenvalues.

1. The eigenvalues of $\hat{\mathbf{J}}^2$ are not negative.

Proof: Let $\hat{\mathbf{J}}^2 |\Psi\rangle = \alpha |\Psi\rangle$. Then

$$\alpha = \langle \Psi | \hat{\mathbf{J}}^2 | \Psi \rangle = \langle \Psi_x | \Psi_x \rangle + \langle \Psi_y | \Psi_y \rangle + \langle \Psi_z | \Psi_z \rangle \ge 0$$

where $|\Psi_i\rangle := \hat{J}_i |\Psi\rangle$ and thus $\langle \Psi_i | = \langle \Psi | \hat{J}_i$, as \hat{J}_i is hermitian. \Box

Therefore we can write the eigenvalues as

$$\hat{\mathbf{J}}^2 |\Psi\rangle = j(j+1)\hbar^2 |\Psi\rangle \text{ and } \hat{J}_z |\Psi\rangle = m\hbar |\Psi\rangle$$

where we temporarily allow $j \in \mathbb{R}^+$ and $m \in \mathbb{R}$ (they will turn out to be half-integer numbers later).

2. Consider $|\Psi_+\rangle = \hat{J}_+ |\Psi\rangle$. We find

$$\begin{split} \langle \Psi_+ | \Psi_+ \rangle &= \langle \Psi | \hat{J}_- \hat{J}_+ | \Psi \rangle = \langle \Psi | \hat{J}_x^2 + \hat{J}_y^2 + \mathbf{i} [\hat{J}_x, \hat{J}_y] | \Psi \rangle = \langle \Psi | \hat{\mathbf{J}}^2 - \hat{J}_z^2 - \hbar \hat{J}_z | \Psi \rangle \\ &= [j(j+1) - m^2 - m] \hbar^2 \end{split}$$

Thus

- (a) $|\Psi_+\rangle = |\text{null}\rangle \Leftrightarrow m = j \text{ or } m = -j 1$
- (b) For m > j or m < -j 1 we would find $\langle \Psi_+ | \Psi_+ \rangle < 0$. Thus $-j 1 \le m \le j$ is required.
- (c) $|\Psi_+\rangle$ is also eigenstate of $\hat{\mathbf{J}}^2$ and \hat{J}_z with the eigenvalues $j(j+1)\hbar^2$ and $(m+1)\hbar$. **Proof:**

$$\hat{\mathbf{J}}^{2}|\Psi_{+}\rangle = \hat{\mathbf{J}}^{2}\hat{J}_{+}|\Psi\rangle = \hat{J}_{+}\hat{\mathbf{J}}^{2}|\Psi\rangle = \hat{J}_{+}j(j+1)\hbar^{2}|\Psi\rangle = j(j+1)\hbar^{2}|\Psi_{+}\rangle$$
$$\hat{J}_{z}|\Psi_{+}\rangle = \hat{J}_{z}(\hat{J}_{x} + \mathrm{i}\hat{J}_{y})|\Psi\rangle = (\hat{J}_{x} + \mathrm{i}\hat{J}_{y})\hat{J}_{z}|\Psi\rangle + \left([\hat{J}_{z},\hat{J}_{x}] + \mathrm{i}[\hat{J}_{z},\hat{J}_{y})]\right)|\Psi\rangle$$
$$= (\hat{J}_{x} + \mathrm{i}\hat{J}_{y})m\hbar|\Psi\rangle + \hbar\left(\mathrm{i}\hat{J}_{y} + \hat{J}_{x}\right)\Psi\rangle = (m+1)\hbar|\Psi_{+}\rangle \qquad \Box$$

58

3.2. ALGEBRA OF ANGULAR MOMENTUM

Now we write $|\Psi\rangle = |a, j, m\rangle$, where a denotes further quantum numbers, as there can be several states with equal j and m. Using (a) and (c) we define for $m \neq j$

$$|a, j, m+1\rangle = \frac{1}{\hbar\sqrt{j(j+1) - m(m+1)}}\hat{J}_{+}|a, j, m\rangle$$
 (3.4)

The repeated operation of \hat{J}_+ provides a sequence of states $|a, j, m\rangle$, $|a, j, m+1\rangle$, $|a, j, m+2\rangle$,.... This sequence stops if $m + i_+ = j$, as in this case $\hat{J}_+|a, j, m+i_+\rangle = 0$. If the sequence does not terminate one reaches states contradicting (b) for i > j - m. The necessity to stop provides us with the condition that $m = j - i_+$ with $i_+ \in \mathbb{N}_0$ holds.

- 3. Consider $|\Psi_{-}\rangle = \hat{J}_{-}|\Psi\rangle$. Now we find $\langle \Psi_{-}|\Psi_{-}\rangle = \hbar^{2}[j(j+1) m^{2} + m]$ implying
 - (a) $|\Psi_{-}\rangle = |\text{null}\rangle \Leftrightarrow m = -j \text{ or } m = j+1$
 - (b) For m < -j or m > j + 1 we would find $\langle \Psi_{-} | \Psi_{-} \rangle < 0$. Thus $-j \le m \le j + 1$ holds.
 - (c) $|\Psi_{-}\rangle$ is also eigenstate of $\hat{\mathbf{J}}^{2}$ and \hat{J}_{z} with eigenvalues $j(j+1)\hbar^{2}$ and $(m-1)\hbar$.

For $m \neq -j$ we define

$$|a, j, m-1\rangle = \frac{1}{\hbar\sqrt{j(j+1) - m(m-1)}}\hat{J}_{-}|a, j, m\rangle$$
 (3.5)

Now the repeated operation of \hat{J}_{-} provides a sequence of states $|a, j, m\rangle$, $|a, j, m - 1\rangle$, $|a, j, m - 2\rangle$,.... This sequence stops if $m - i_{-} = -j$ holds, as $\hat{J}_{-}|a, j, m - i_{-}\rangle = 0$ in this case. Otherwise the state $|a, j, m - i\rangle$ contradicts (b) for i > -j + m. Thus $m = -j + i_{-}$ holds with $i_{-} \in \mathbb{N}_{0}$.

Summary of 2 and 3:

For each common eigenstate $|\Psi\rangle$ of $\hat{\mathbf{J}}^2$ and \hat{J}_z with eigenvalues $j(j+1)\hbar^2$ and $m\hbar$ holds:

• There are $i_+, i_- \in \mathbb{N}_0$ with $m+i_+ = j$ and $m-i_- = -j$. $\Rightarrow 2j = i_++i_- \in \mathbb{N}_0$

• Repeated operation of \hat{J}_+ and \hat{J}_- creates a sequence of states $|a, j, m'\rangle$ with $m' = -j, -j + 1, \ldots j$, which are all common eigenstates of $\hat{\mathbf{J}}^2$ and \hat{J}_z .

The results of the points 1, 2, and 3 can be summarized:

The operator $\hat{\mathbf{J}}^2$ have the eigenvalues $j(j+1)\hbar^2$ with $j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \ldots$ The corresponding eigenstates form *multiplets* \mathcal{M}^j of 2j + 1 states $|j, m\rangle$ with $m = -j, -j + 1, \ldots j$, which are eigenstates of \hat{J}_z with the respective eigenvalue $m\hbar$ I.e.,

$$\mathbf{J}^{2}|j,m\rangle = j(j+1)\hbar^{2}|j,m\rangle \quad \text{and} \quad J_{z}|j,m\rangle = m\hbar|j,m\rangle$$
(3.6)

3.2.2 Implication for systems with rotational symmetry

Now we want to consider the Hamilton-operator in a rotated system. For this purpose we consider the matrix element $\langle \Psi_1 | \hat{H} | \Psi_2 \rangle$ and rotate all states by \hat{U}_R resulting in $\langle \Psi'_1 | \hat{H} | \Psi'_2 \rangle = \langle \Psi_1 | \hat{U}_R^{\dagger} \hat{H} \hat{U}_R | \Psi_2 \rangle$. If the system described by the Hamiltonian is rotational invariant, $\langle \Psi'_1 | \hat{H} | \Psi'_2 \rangle = \langle \Psi_1 | \hat{H} | \Psi_2 \rangle$ must hold for arbitrary states $|\Psi_1\rangle, |\Psi_2\rangle$. This directly implies the identity $\hat{U}_R^{\dagger} \hat{H} \hat{U}_R = \hat{H}$. Considering infinitesimal rotations around the axis j, we have $\hat{U}_R = 1 - i\delta\varphi \hat{J}_j/\hbar + \mathcal{O}\{\delta\varphi^2\}$ and

$$\hat{U}_R^{\dagger}\hat{H}\hat{U}_R = \hat{H} - \frac{\mathrm{i}}{\hbar}\delta\varphi[\hat{H}, \hat{J}_j] + \mathcal{O}\{\delta\varphi^2\}$$

Thus we obtain the important relation:

System is invariant under rotation
$$j$$
-axis $\Leftrightarrow [\hat{H}, \hat{J}_j] = 0$ (3.7)

which relates the commutation relations of the Hamilton operator with the angular momentum to the rotational invariance of the system.

Consequently, the Hamilton-operator \hat{H} has rotational symmetry around all axis, if $[\hat{H}, \hat{J}_i] = 0$ for all i = x, y, z and we also find $[\hat{H}, \hat{\mathbf{J}}^2] = 0$. Therefore there exists a system of common eigenstates for the operators $\hat{H}, \hat{\mathbf{J}}^2$ and \hat{J}_z with respective eigenvalues $E, j(j+1)\hbar^2$ and $m\hbar$. For such an eigenstate $|\Psi\rangle$, we can construct $|\Psi_{\pm}\rangle = \hat{J}_{\pm}|\Psi\rangle$ and find $\hat{H}|\Psi_{\pm}\rangle = \hat{H}\hat{J}_{\pm}|\Psi\rangle = \hat{J}_{\pm}\hat{H}|\Psi\rangle = \hat{J}_{\pm}E|\Psi\rangle = E|\Psi_{\pm}\rangle$. Thus $|\Psi_{\pm}\rangle$ are eigenstates of \hat{H} with the same energy. Repeating this procedure we find:

60

In systems with rotational symmetry around all spatial axis, there is a complete set of common eigenstates $|n, j, m\rangle$ for \hat{H} , \hat{J}^2 , and \hat{J}_z . For given j, the multiplets \mathcal{M}^j with $m = -j, -j+1, \ldots j$ have the identical energy. This provides a (2j+1)fold degeneracy.

The index n is commonly used to distinguish states with the same j and m, but different eigenvalues E_{nj} of \hat{H} .

Example: The isotropic three-dimensional harmonic oscillator has a non-degenerate ground state with energy $3\hbar\omega/2$ and a three-fold degenerate first excited state with energy $5\hbar\omega/2$. Which z-components of the angular momentum can be measured in the respective states?

The isotropic three-dimensional harmonic oscillator has rotational symmetry around all spatial axis. Thus a non-degenerate state must belong to a multiplet \mathcal{M}^0 , and the only possible eigenvalues of \hat{L}_z is zero. For the first excited state, the three-fold degeneracy is a \mathcal{M}^1 multiplet (without further arguing, we could not exclude the alternative case of three \mathcal{M}^0 multiplets, which accidentally have the same energy, but this is not the case). Thus one can measure a z-component of $-\hbar$, 0, or \hbar for the angular momentum.

3.2.3 Example: Matrix representation of the angular momentum operators

Deuteron (a bound state between a neutron and a proton) is a nucleus with spin 1. This means the bound state is three-fold degenerate forming a \mathcal{M}^1 multiplet. The three basis states $|j = 1, m = 1\rangle$, $|j = 1, m = 0\rangle$, and $|j = 1, m = -1\rangle$ span a three-dimensional space of possible states for the deuteron nucleus.

Task: Find the matrix representations for the operators $\hat{J}_x, \hat{J}_y, \hat{J}_z$, and \hat{J}^2 in this space.

Let us use the following matrix representations of the basis vectors $|j = 1, m\rangle$

$$|1,1\rangle \leftrightarrow \begin{pmatrix} 1\\0\\0 \end{pmatrix} \quad |1,0\rangle \leftrightarrow \begin{pmatrix} 0\\1\\0 \end{pmatrix} \quad |1,-1\rangle \leftrightarrow \begin{pmatrix} 0\\0\\1 \end{pmatrix}$$

The columns of the respective matrices for an operator result from the action of the operators on the basis vectors. Let us start with \hat{J}_{-} . Using Eq. (3.5) we find

$$\hat{J}_{-}|1,1\rangle = \sqrt{(1+1)(1-1+1)}\hbar|1,0\rangle = \sqrt{2}\hbar|1,0\rangle \leftrightarrow \sqrt{2} \begin{pmatrix} 0\\1\\0 \end{pmatrix}$$

and similarly

$$\hat{J}_{-}|1,0\rangle = \sqrt{2}\hbar|1,-1\rangle \leftrightarrow \sqrt{2} \begin{pmatrix} 0\\0\\1 \end{pmatrix} \qquad \hat{J}_{-}|1,-1\rangle = 0 \leftrightarrow \begin{pmatrix} 0\\0\\0 \end{pmatrix}$$

Putting the columns together provides the matrix representation of \hat{J}_{-}

$$\hat{J}_{-} \leftrightarrow \hbar \begin{pmatrix} 0 & 0 & 0\\ \sqrt{2} & 0 & 0\\ 0 & \sqrt{2} & 0 \end{pmatrix}$$

As $\hat{J}_{+} = \hat{J}_{-}^{\dagger}$, the matrix of \hat{J}_{+} is just the transposed (and conjugated) matrix, due to Eq. (1.10). From the matrices of \hat{J}_{\pm} we get directly the matrix representations of \hat{J}_{x} and \hat{J}_{y} :

$$\begin{split} \hat{J}_x &= \frac{1}{2}(\hat{J}_+ + \hat{J}_-) \leftrightarrow \frac{\hbar}{2} \begin{pmatrix} 0 & \sqrt{2} & 0\\ \sqrt{2} & 0 & \sqrt{2}\\ 0 & \sqrt{2} & 0 \end{pmatrix} \\ \hat{J}_y &= \frac{i}{2}(\hat{J}_- - \hat{J}_+) \leftrightarrow \frac{i\hbar}{2} \begin{pmatrix} 0 & -\sqrt{2} & 0\\ \sqrt{2} & 0 & -\sqrt{2}\\ 0 & \sqrt{2} & 0 \end{pmatrix} \end{split}$$

From the eigenvalue relations $\hat{J}_z|1,m\rangle = \hbar m|1,m\rangle$ we get

$$\hat{J}_z \leftrightarrow \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

and \hat{J}^2 is proportional to the identity operator as all three states have the same eigenvalue $j(j+1)\hbar^2 = 2\hbar^2$.

$$\hat{J}^2 \leftrightarrow 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

3.3 Spin angular momentum

The angular momentum of charged particles is proportional to its magnetic moment. The Stern-Gerlach experiment reveals two different measurement values for the z-component of the magnetic moment for silver atoms (and several other atoms). Also by spectroscopical methods, a double degeneracy of the electron states, which is lifted by a magnetic field, can be observed in many systems. In terms of angular momentum, a doublet is a multiplet $\mathcal{M}^{1/2}$ and the data can be explained by assigning an internal angular momentum with j = 0.5 to the electron. This property is called *electron spin* and was originally postulated by Goudsmith and Uhlenbeck in 1925.

3.3.1 Algebra and matrix representation

The angular momentum operators operators \hat{J} referring to the spin are commonly denoted by \hat{S} , which we use in the following. Because spin is an angular momentum, it has the algebra of angular momentum, so everything we discussed in the previous section can directly be applied to \hat{S} . We denote the two possible eigenstates of \hat{S}_z with eigenvalues $m_s \hbar = \pm \hbar/2$ by $|\uparrow\rangle$ and $|\downarrow\rangle$, respectively. As motivated above, the electron has an internal degree of freedom in a two-dimensional space spanned by the eigenstates $|\uparrow\rangle$ and $|\downarrow\rangle$ of the operator \hat{S}_z with eigenvalues $m_j = \pm 1/2$, repectively. In this basis a general state can be written as a column (*Spinor*):

$$|a\rangle = a_{\uparrow}|\uparrow\rangle + a_{\downarrow}|\downarrow\rangle \to \begin{pmatrix} a_{\uparrow} \\ a_{\downarrow} \end{pmatrix}$$
(3.8)

Let $\hat{S}_x, \hat{S}_y, \hat{S}_z$ be the angular momentum operators in spin space. From the general properties (3.4,3.5, and 3.6) we find

$$\hat{S}_{z}|\uparrow\rangle = \frac{1}{2}\hbar|\uparrow\rangle \qquad \qquad \hat{S}_{z}|\downarrow\rangle = -\frac{1}{2}\hbar|\downarrow\rangle \\ \hat{S}_{+}|\uparrow\rangle = 0 \qquad \qquad \hat{S}_{+}|\downarrow\rangle = \hbar|\uparrow\rangle \\ \hat{S}_{-}|\uparrow\rangle = \hbar|\downarrow\rangle \qquad \qquad \hat{S}_{-}|\downarrow\rangle = 0$$

In the basis $|\uparrow\rangle$ and $|\downarrow\rangle$, the spin operators are therefore represented by the following matrices

$$\hat{S}_z \to \frac{\hbar}{2} \begin{pmatrix} 1 & 0\\ 0 & -1 \end{pmatrix} \quad \hat{S}_+ \to \hbar \begin{pmatrix} 0 & 1\\ 0 & 0 \end{pmatrix} \quad \hat{S}_- \to \hbar \begin{pmatrix} 0 & 0\\ 1 & 0 \end{pmatrix}$$

As $\hat{S}_x = (\hat{S}_+ + \hat{S}_-)/2$ and $\hat{S}_y = (\hat{S}_+ - \hat{S}_-)/2i$ we obtain

the representation of the spin in the space
$$\mathcal{M}^{1/2}$$
 is given by
 $\hat{\mathbf{S}} = \hat{S}_x \mathbf{e}_x + \hat{S}_y \mathbf{e}_y + \hat{S}_z \mathbf{e}_z \to \frac{\hbar}{2} \boldsymbol{\sigma}$
with the Pauli matrices $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \sigma_y = \begin{pmatrix} 0 & -\mathbf{i} \\ \mathbf{i} & 0 \end{pmatrix} \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

Note that **S** and σ are vectors in the conventional three-dimensional real space, with a direction pointing along the axis of rotation they generate. In contrast the columns in Eq. (3.8) and the Pauli matrices are elements of the two-dimensional complex spin space.³

3.3.2 Spin precession in a magnetic field

Spins with mass m are commonly associated with a magnetic moment as

$$\hat{\boldsymbol{\mu}} = -g \frac{e}{2m_e} \hat{\mathbf{S}}$$
(3.9)

for electrons as well as atoms, ions, and molecules, where the electrons turn out to be most relevant and

$$\hat{\boldsymbol{\mu}} = g \frac{e}{2m_p} \hat{\mathbf{S}} \tag{3.10}$$

³Here we refrain from writing the vectors $\hat{\mathbf{S}}$ and $\boldsymbol{\sigma}$ as columns (or rows) with three elements (which is actually a representation) in order to avoid confusion with the two-dimensional spin space.

for nuclei. Here e > 0 is the elementary charge, m_e the electron mass and m_p the proton mass. The gyromagnetic ratio (or g-factor) depends on the particle: For electrons the value $g_e = 2.0023...^4$ results from relativistic quantum electrodynamics (the electron spin is a central feature in the formulation of relativistic quantum mechanics, while it appears more artificially in the nonrelativistic Schrödinger equation). For atoms, ions, and molecules, the orbital parts of the electron may also play a role, providing g-factors between one and two. For protons $g_p = 5.5883...$ is relatively large and neutrons have $g_n = -3.8263...$ although they are electrically neutral. Nevertheless, note that the nuclear magnetic moments are generally three orders of magnitude lower than the electron ones due to the large proton mass.

The interaction energy of a magnetic moment with a magnetic field is $-\mu \cdot \mathbf{B}$. For an electronic spin we obtain the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle \quad \text{with} \quad \hat{H} = g_e \frac{e}{2m_e} \mathbf{B} \cdot \hat{\mathbf{S}}$$
(3.11)

Using the common representation of the spin in the space $\mathcal{M}^{1/2}$, we find

$$i\hbar \begin{pmatrix} \dot{a} \\ \dot{b} \end{pmatrix} = g_e \frac{e\hbar}{4m_e} \begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix}$$

If the magnetic field is in the z- direction this equation is uncoupled, and the solution can easily be written down:

$$\begin{pmatrix} a(t) \\ b(t) \end{pmatrix} = \begin{pmatrix} a(0)e^{-i\omega_L t/2} \\ b(0)e^{i\omega_L t/2} \end{pmatrix} \quad \text{with the Larmor frequency } \omega_L = \frac{g_e eB}{2m_e}$$

At this stage, the choice of ω_L is surprising as the time $4\pi/\omega$, i.e., two cycles, is needed to return to the original state. Things are however different for the expectation values of the main observables:

$$\begin{split} \langle \Psi | \hat{S}_z | \Psi \rangle &= \begin{pmatrix} a^*(t) & b^*(t) \end{pmatrix} \begin{pmatrix} \hbar/2 & 0 \\ 0 & -\hbar/2 \end{pmatrix} \begin{pmatrix} a(t) \\ b(t) \end{pmatrix} = \frac{\hbar}{2} (|a(t)|^2 - |b(t)|^2) \\ &= \frac{\hbar}{2} (|a(0)|^2 - |b(0)|^2) \end{split}$$

⁴This quantity could recently be measured with a remarkable accuracy of 7.6 parts in 10^{13} , B. Odom *et al.*, Phys. Rev. Lett. **97** 030801 (2006)

Figure 3.2: Precession of the classical spinning top. The torque acted on the spinning top by the gravitation points in the same direction as $\mu \times B\mathbf{e}_z$ for an electronic spin in a magnetic field pointing upwards. (Figure from Xavier Snelgrove, Wikipedia)



Not surprising, $\langle \Psi | \hat{S}_z | \Psi \rangle$ is constant in time as the magnetic field is in the z-direction. Similarly we obtain

$$\langle \Psi | \hat{S}_x | \Psi \rangle = \begin{pmatrix} a^*(t) & b^*(t) \end{pmatrix} \begin{pmatrix} 0 & \hbar/2 \\ \hbar/2 & 0 \end{pmatrix} \begin{pmatrix} a(t) \\ b(t) \end{pmatrix} = \frac{\hbar}{2} (a^*(t)b(t) + a(t)b^*(t))$$
$$= \hbar \operatorname{Re}\{a^*(0)b(0)e^{\mathrm{i}\omega_L t}\} = \hbar A\cos(\omega_L t + \alpha)$$

for $a^*(0)b(0) = Ae^{i\alpha}$ and finally $\langle \Psi | \hat{S}_y | \Psi \rangle = \hbar A \sin(\omega_L t + \alpha)$. The motion of $\langle \Psi | \hat{\mathbf{S}} | \Psi \rangle$ is called *precession*. This motion is such that the projection on the $x - y - \beta$ plane is moving along a circle with constant angular velocity like a spinning top, see Fig. 3.2. Note, however, that $\langle \Psi | \hat{S}_x | \Psi \rangle$ is the *expectation value* for the measurement of the x-component of the spin. The actual measurement values are the eigenvalues of the operator \hat{S}_x , which are $\pm \hbar/2$ (see section 1.2.5).

3.4 Addition of angular momentum

I will start by giving some precise definitions and the main results. These might seem a bit "dry" in the beginning, but this will allow you to recognize the important results in the rest of the chapter.

3.4.1 Sum of angular momenta

Suppose we have two distinct angular momentum operators J_1 and J_2 . These could for example be
- A particle's spin and it's orbital angular momentum
- Two particles with spins $S_1 = J_1$ and $S_2 = J_2$

Because J_1 and J_2 are angular momentum operators, their components $J_{1,2i}$ are Hermitian and they satisfy the angular momentum algebra. We assume operators J_1 and J_2 each operate in different Hilbert spaces, J_1 operates in \mathcal{V}_1 and J_2 operates in \mathcal{V}_2 .

The sum of angular momenta J_1 and J_2 is an angular momentum J that operates in the product space $\mathcal{V} = \mathcal{V}_1 \otimes \mathcal{V}_2$

$$J_i = J_1 \otimes \mathbb{I} + \mathbb{I} \otimes J_2$$
, Hermitian, with $[J_i, J_j] = i\varepsilon_{ijk}\hbar J_k$ (3.12)

where \mathbb{I} is the identity operator.

Remark that we often (read most of the time) just write $J = J_1 + J_2$, but remember that J_i only acts on \mathcal{V}_i . This implies that $[J_1, J_2] = [J_1 \otimes \mathbb{I}, \mathbb{I} \otimes J_2] = 0 = [J_2, J_1]$. Therefore

$$[J_i, J_j] = [J_{1i} \otimes \mathbb{I} + \mathbb{I} \otimes J_{2i}, J_{1j} \otimes \mathbb{I} + \mathbb{I} \otimes J_{2j}]$$
(3.13)

$$= [J_{1i} \otimes \mathbb{I}, \ J_{1j} \otimes \mathbb{I}] + [\mathbb{I} \otimes J_{2i}, \ \mathbb{I} \otimes J_{2j}]$$

$$(3.14)$$

$$= [J_{1i}, J_{1j}] \otimes \mathbb{I} + \mathbb{I} \otimes [J_{2i}, J_{2j}]$$

$$(3.15)$$

$$= i\varepsilon_{ijk}\hbar J_{1k} \otimes \mathbb{I} + \mathbb{I} \otimes i\varepsilon_{ijk}\hbar J_{2k}$$
(3.16)

$$= i\varepsilon ijk\hbar \left(J_{1k} \otimes \mathbb{I} + \mathbb{I} \otimes J_{2k}\right) \tag{3.17}$$

$$=i\varepsilon_{ijk}\hbar J_k \tag{3.18}$$

Now one obvious complete set of commuting operators (CSCO) for this system is $\{H, J_1^2, J_{1z}, J_2^2, J_{2z}\}$, which is just an extension of what we did before, but now taking into account both angular momenta (this turns out to be not quite true, but we'll see this when studying spin-orbit coupling). We now want to find a complete set of commuting observables in which we can include the total angular momentum operator. Now note that

$$J^2 = J_1^2 + J_2^2 + 2J_1 \cdot J_2 \tag{3.19}$$

$$= J_1^2 + J_2^2 + J_{1+}J_{2-} + J_{1-}J_{2+} + 2J_{1z}J_{2z}$$
(3.20)

The last term on the right hand side in (3.19) can be written like this because we know that J_1 and J_2 commute, and in (3.20) we used properties of the step/shift operators that were discussed earlier in this chapter. We see that there now is a coupling term between J_1 and J_2 and this implies that if we want to have J^2 in our CSCO, we can not have J_{1z} and J_{2z} in it anymore, because $[J_1 \cdot J_2, J_{1,2z}] \neq 0$. Because generally for angular momentum we have that $[J^2, J_i] = 0$, we see here that J_1^2 and J_2^2 do still commute with J^2 . So we can start a CSCO with $\{J^2, J_1^2, J_2^2\}$, but we will need one more angular momentum operator. ⁵ Because for general angular momentum operator J_z must be the fourth angular momentum operator for our CSCO.

This means we have not two distinct bases that span the same vector space \mathcal{V} . The vectors that span these two bases will be written $|j_1m_1j_2m_2\rangle$ and $|jm\rangle$ (short for $|jmj_1j_2\rangle$). The coefficients that determine the passage between these two bases are called the Clebsch-Gordon coefficients,

$$|j\,m\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} \langle j_1\,m_1\,j_2\,m_2|jm\rangle |j_1\,m_1\,j_2\,m_2\rangle$$
(3.21)
(3.22)

where the Clebsch-Gordon coefficients are $CB(j, m, j_1, j_2, m_1, m_2) = \langle j_1 m_1 j_2 m_2 | jm \rangle$. The quantum number j of total angular momentum obeys

$$j = j_1 \otimes j_2 = j_1 + j_2 \oplus j_1 + j_2 - 1 \oplus \dots \oplus |j_1 - j_2|$$
(3.23)

meaning that taking the product space of two angular momenta j_1 and j_2 gives rise to different multiplets with total angular moment j. The total magnetic moment m must obey

$$m = m_1 + m_2 \tag{3.24}$$

⁵ Note that here we did not include H, our Hamiltonian in the CSCO, but it must actually be there to determine the principle quantum number n. For a system with a central potential this number's given by solving the radial equation, as we've seen before. Here we concentrate on angular momentum, but when including coupling terms between J_1 and J_2 in the Hamiltonian we must take a closer look at the CSCO again.

this is quite easy to see as the eigenvalues for J_{1z} and J_{2z} are linear. It's important to note that the total angular momentum $j \neq j_1 + j_2$ (there's only one multiplet that has this property, but there are other multiplets with other j).

Example: for $j_1 = \frac{3}{2}$ and $j_2 = \frac{1}{2}$, one has $j \in \left\{\frac{5}{2}, \frac{3}{2}, \frac{1}{2}\right\}$.

3.4.2 Two spin one-half particles

The spin operator $S = (S_x, S_y, S_z)$ is Hermitian and satisfies the angular momentum algebra. In fact, there are only two types of angular momentum, orbital angular momentum and spin angular momentum. Orbital angular momentum acts on spatial degrees of freedom, whereas spin angular momentum only acts on spin degrees of freedom. Spin angular momentum is said to be an intrinsic property of particles (Fermions in fact). Here we will write eigenvalues equations as

$$S^{2}|s, m\rangle = \hbar^{2}s(s+1)|s, m\rangle = \frac{3}{4}\hbar^{2}|\frac{1}{2}, \pm \frac{1}{2}\rangle$$
 (3.25)

$$S_z|s, m\rangle = \hbar|s, m\rangle = \pm \frac{\hbar}{2}|\frac{1}{2}, \pm \frac{1}{2}\rangle$$
(3.26)

with $s = \frac{1}{2}$ and $m = \pm \frac{1}{2}$ (spin up +, spin down -).⁶

Eigenbasis for total angular momentum

For two spin- $\frac{1}{2}$ particles, the product space $\mathcal{V}_1 \otimes \mathcal{V}_2$ is four dimensional, spanned by the vectors

$$|+\rangle_1 \otimes |+\rangle_2, \, |+\rangle_1 \otimes |-\rangle_2, \, |-\rangle_1 \otimes |+\rangle_2, \, |-\rangle_1 \otimes |-\rangle_2, \tag{3.27}$$

Note that I here labeled particle one and particle two, so I suppose that I know which is which. This is of course not true in general, but we here keep the convention that the left hand vector space is for particle one, the right vector space for particle two, even if I don't always specify the labels. The total spin angular momentum operator is written

$$S = S_1 + S_2 = S_1 \otimes \mathbb{I} + \mathbb{I} \otimes S_2.$$
(3.28)

⁶ Note that I often use shorter but equivalent notation: $|\frac{1}{2}\frac{1}{2}\rangle = |\uparrow\rangle = |+\rangle$ and $|\frac{1}{2} - \frac{1}{2}\rangle = |\downarrow\rangle$ $\rangle = |-\rangle$.

The first important question to answer in order to understand what's happening is the following; What are the eigenvalues of $S_z = S_{1z} + S_{2z}$? We see that

$$S_{z}(|\frac{1}{2},\frac{1}{2}\rangle \otimes |\frac{1}{2},\frac{1}{2}\rangle) = S_{1z}|\frac{1}{2},\frac{1}{2}\rangle \otimes |\frac{1}{2},\frac{1}{2}\rangle + |\frac{1}{2},\frac{1}{2}\rangle \otimes S_{2z}|\frac{1}{2},\frac{1}{2}\rangle$$

$$= \hbar(|\frac{1}{2},\frac{1}{2}\rangle \otimes |\frac{1}{2},\frac{1}{2}\rangle), \text{ so } m = 1 \qquad (3.29)$$

$$S_{z}(|\frac{1}{2},\frac{1}{2}\rangle \otimes |\frac{1}{2},-\frac{1}{2}\rangle) = S_{1z}|\frac{1}{2},\frac{1}{2}\rangle \otimes |\frac{1}{2},-\frac{1}{2}\rangle + |\frac{1}{2},\frac{1}{2}\rangle \otimes S_{2z}|\frac{1}{2},-\frac{1}{2}\rangle$$

$$= 0 \quad \text{so } m = 0 \qquad (3.30)$$

$$S_{z}(|\frac{1}{2},-\frac{1}{2}\rangle \otimes |\frac{1}{2},\frac{1}{2}\rangle) = S_{1z}|\frac{1}{2},-\frac{1}{2}\rangle \otimes |\frac{1}{2},\frac{1}{2}\rangle + |\frac{1}{2},-\frac{1}{2}\rangle \otimes S_{2z}|\frac{1}{2},\frac{1}{2}\rangle$$

$$= 0, \quad \text{so } m = 0 \qquad (3.31)$$

$$S_{z}(|\frac{1}{2},-\frac{1}{2}\rangle \otimes |\frac{1}{2},-\frac{1}{2}\rangle) = S_{1z}|\frac{1}{2},-\frac{1}{2}\rangle \otimes |\frac{1}{2},-\frac{1}{2}\rangle + |\frac{1}{2},-\frac{1}{2}\rangle \otimes S_{2z}|\frac{1}{2},-\frac{1}{2}\rangle$$

$$= -\hbar(|\frac{1}{2},\frac{1}{2}\rangle \otimes |\frac{1}{2},\frac{1}{2}\rangle), \quad \text{so } m = -1 \qquad (3.32)$$

We see that simply $m = m_1 + m_2$, as expected from the fact that the eigenvalues of S_z are linear in m. Because total angular momentum satisfies all general properties of angular momentum we have here that $m \in [[-j, j]]$, so we have at least one multiplet with j = 1, meaning that $m \in \{1, 0, -1\}$, so this gives us a triplet. Our product space is spanned by four vectors, so there must be one more vector to find, this is a singlet state with j = 0 and m = 0. We will write these states using the usual notation for angular momentum as

$$\{|1,1\rangle, |1,0\rangle, |1,-1\rangle\} \quad \text{Triplet} \tag{3.33}$$

$$\{|0,0\rangle\} \qquad \text{Singlet} \qquad (3.34)$$

It can be seen, as given in the previous paragraph, that one can write $\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0$. In terms of number of states one could write $2 \times 2 = 3+1$, meaning that two vector spaces of dimension 2 each give rise to two multiplets, one of multiplicity 3 (triplet) and one of multiplicity one (singlet). The thing to do now is to find how these two basis are related. One can easily convince oneself that the states with largest magnetic moments $|1, 1\rangle$ and $|1, -1\rangle$ are just,

$$|1, 1\rangle = \left|\frac{1}{2}, \frac{1}{2}\right\rangle \otimes \left|\frac{1}{2}, \frac{1}{2}\right\rangle = |+\rangle \otimes |+\rangle, \qquad (3.35)$$

$$|1, -1\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle \otimes |\frac{1}{2}, -\frac{1}{2}\rangle = |-\rangle \otimes |-\rangle, \qquad (3.36)$$

(3.37)

The third state of the triplet and the singlet state can be expected to be some linear combination of the two states that are left over. We thus have do determine

$$|1, 0\rangle = a |\frac{1}{2}, \frac{1}{2}\rangle \otimes |\frac{1}{2}, -\frac{1}{2}\rangle + b |\frac{1}{2}, -\frac{1}{2}\rangle \otimes |\frac{1}{2}, \frac{1}{2}\rangle$$
(3.38)

$$|0, 0\rangle = c|\frac{1}{2}, \frac{1}{2}\rangle \otimes |\frac{1}{2}, -\frac{1}{2}\rangle + d|\frac{1}{2}, -\frac{1}{2}\rangle \otimes |\frac{1}{2}, \frac{1}{2}\rangle$$
(3.39)

with the condition that $|1, 0\rangle$ and $|0, 0\rangle$ are orthogonal. We can find $|1, 0\rangle$ easily by operating on $|1, 1\rangle$ with the step/shift operator, satisfying

$$S_{\pm}|s, m\rangle = \hbar \sqrt{s(s+1) - m(m\pm 1)}|s, m\pm 1\rangle.$$
 (3.40)

This gives us

$$S_{-}|1,1\rangle = \hbar\sqrt{1(1+1) - 1(1-1)}|1,0\rangle = \sqrt{2}\hbar|1,0\rangle$$
(3.41)

$$= S_{-}(|\frac{1}{2}, \frac{1}{2}\rangle \otimes |\frac{1}{2}, \frac{1}{2}\rangle)$$
(3.42)

$$=S_{1-}|\frac{1}{2},\frac{1}{2}\rangle\otimes|\frac{1}{2},\frac{1}{2}\rangle+|\frac{1}{2},\frac{1}{2}\rangle\otimes S_{2-}|\frac{1}{2},\frac{1}{2}\rangle$$
(3.43)

$$=\hbar(|\frac{1}{2}, -\frac{1}{2}\rangle \otimes |\frac{1}{2}, \frac{1}{2}\rangle + |\frac{1}{2}, \frac{1}{2}\rangle \otimes |\frac{1}{2}, -\frac{1}{2}\rangle)$$
(3.44)

We conclude that

$$|1, 0\rangle = \frac{1}{\sqrt{2}} \left(|\frac{1}{2}, -\frac{1}{2}\rangle \otimes |\frac{1}{2}, \frac{1}{2}\rangle + |\frac{1}{2}, \frac{1}{2}\rangle \otimes |\frac{1}{2}, -\frac{1}{2}\rangle \right)$$
(3.45)

And because $|0, 0\rangle$ has to be orthogonal it can be written

$$|0, 0\rangle = \frac{1}{\sqrt{2}} \left(-|\frac{1}{2}, -\frac{1}{2}\rangle \otimes |\frac{1}{2}, \frac{1}{2}\rangle + |\frac{1}{2}, \frac{1}{2}\rangle \otimes |\frac{1}{2}, -\frac{1}{2}\rangle \right)$$
(3.46)

where we used the same sign convention as in the Clebsch-Gordon tables. The question now is if the states we just found are indeed eigenstates of the operator S^2 . We verified in class that $|0, 0\rangle$ is indeed eigenstate with eigenvalue zero, and it's a good exercise to do it yourself for the triplet states. To do this one has to use the identity

$$S^2 = S_1^2 + S_2^2 + 2S_1 \cdot S_2 \tag{3.47}$$

$$= S_1^2 + S_2^2 + 2(S_{1x}S_{2x} + S_{1y}S_{2y} + S_{1z}S_{2z})$$
(3.48)

$$= S_1^2 + S_2^2 + S_{1+}S_{2-} + S_{1-}S_{2+} + 2S_{1z}S_{2z}$$
(3.49)

Now what if our two particles are indistinguishable? Well, the spin statistics theorem loosely tells us the following:

Under the exchange of indistinguishable particles the wave function must be:

- symmetric for integer spin particles (bosons)
- anti-symmetric for half-spin particles (fermions)

We will not give a proof of this theorem here, but we'll work with to analyze our singlet and triplet spin- $\frac{1}{2}$ states. We have to remember that in general we can write the wave function for Fermions as

$$\phi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) = -\phi(\mathbf{r}_2, s_2; \mathbf{r}_1, s_1)$$
(3.50)

so there is a spatial as well as a spin dependence. If we exchange particle one and two in the triplet spin states, it can be seen we get back exactly the same wave function. This means the spatial part of the wave function for the triplet states must be anti-symmetric in order for these states to obey Fermi statistics. It was shown in class that as a consequence the spins in the triplet states can not occupy the same orbital or the same space. This means that, moving in different orbitals, these states have much lower Coulomb energy that the singlet state (that is anti-symmetric in spin space, and symmetric in real space). As stated by one of Hund's rules, the higher the multiplicity, the lower the energy of the states in that multiplet.

Coupling of Two Spins, the Product Space

In order to become acquainted with the addition of angular momenta we consider two spin- $\frac{1}{2}$ - particles. Such a physical system is *positronium*, which consists of one electron (index e) and one positron (index p in this section). If this "atom" is in its ground state the particles are in a relative s- state and do not carry orbital angular momentum. The total angular momentum of the system is given by the two spin operators

$$\hat{\mathbf{S}} = \hat{\mathbf{S}}_e + \hat{\mathbf{S}}_p \tag{3.51}$$

Formally this operator acts on the *product space* of electron and positron spin kets. Generally the product space is a new space of kets, which can be constructed as follows: One chooses a basis for each space. Then the product space is spanned by a basis consisting of all pairings between the basis kets of both spaces. Consequently the dimensions of the product space is the product of the dimension of both spaces. In our case of positronium any ket of the product space (with index ep) can be written as

$$|\Psi\rangle_{ep} = \alpha_1 \underbrace{|\uparrow\rangle_e \otimes |\uparrow\rangle_p}_{=|a_1\rangle_{ep}} + \alpha_2 \underbrace{|\uparrow\rangle_e \otimes |\downarrow\rangle_p}_{=|a_2\rangle_{ep}} + \alpha_3 \underbrace{|\downarrow\rangle_e \otimes |\uparrow\rangle_p}_{=|a_3\rangle_{ep}} + \alpha_4 \underbrace{|\downarrow\rangle_e \otimes |\downarrow\rangle_p}_{=|a_4\rangle_{ep}} \quad (3.52)$$

where the \otimes is the common symbol for this kind of combination. Note that the order really matters, as on the left-hand side of \otimes we have the electron state, while the positron state is located on the right-hand side.

Any type of spin-spin interaction causes the coupling between the spins by an effective Hamiltonian operating on both spin spaces simultaneously. Motivated by the classical interaction between magnetic moments, a typical Hamiltonian is

$$\hat{H} = \frac{U}{\hbar^2} \hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p = \frac{U}{\hbar^2} (\hat{S}_{ex} \hat{S}_{px} + \hat{S}_{ey} \hat{S}_{py} + \hat{S}_{ez} \hat{S}_{pz})$$
(3.53)

where U > 0 if the two particles have opposite charge. Now we want to use the matrix representation with the basis defined in Eq. (3.52). We have to evaluate matrix elements such as

$$\langle a_i | \hat{S}_{ex} \hat{S}_{px} (|\uparrow\rangle_e \otimes |\uparrow\rangle_p) = \frac{\hbar}{2} \langle a_i | \hat{S}_{ex} (|\uparrow\rangle_e \otimes |\downarrow\rangle_p) = \frac{\hbar^2}{4} \langle a_i | (\downarrow\rangle_e \otimes |\downarrow\rangle_p) = \frac{\hbar^2}{4} \delta_{i4}$$

In this way we obtain the first column of the representation

$$\hat{S}_{ex}\hat{S}_{px} \to \frac{\hbar^2}{4} \begin{pmatrix} 0 & 0 & 0 & 1\\ 0 & 0 & 1 & 0\\ 0 & 1 & 0 & 0\\ 1 & 0 & 0 & 0 \end{pmatrix}$$

and the other columns are obtained analogously. Similarly we find

$$\hat{S}_{ey}\hat{S}_{py} \to \frac{\hbar^2}{4} \begin{pmatrix} 0 & 0 & 0 & -1\\ 0 & 0 & 1 & 0\\ 0 & 1 & 0 & 0\\ -1 & 0 & 0 & 0 \end{pmatrix} \quad \hat{S}_{ez}\hat{S}_{pz} \to \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 & 0 & 0\\ 0 & -1 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & 1 \end{pmatrix}$$

This provides the stationary Schrödinger equation $\hat{H}|\Psi\rangle = E|\Psi\rangle$ in matrix representation

$$\frac{U}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix} = E \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix}$$

Thus the eigenvalues E_i and eigenstates $|\Psi_i\rangle$ are obtained by matrix diagonalization. We find a threefold eigenvalue $E_1 = U/4$ with corresponding eigenstates

$$|1,1\rangle = |\uparrow\rangle_{e} \otimes |\uparrow\rangle_{p}$$

$$|1,0\rangle = \frac{1}{\sqrt{2}} \Big(|\uparrow\rangle_{e} \otimes |\downarrow\rangle_{p} + |\downarrow\rangle_{e} \otimes |\uparrow\rangle_{p} \Big)$$
(3.54)

$$|1,-1\rangle = |\downarrow\rangle_{e} \otimes |\downarrow\rangle_{p}$$

and a single eigenvalue $E_0 = -3U/4$ with corresponding eigenstate

$$|0,0\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\rangle_e \otimes |\downarrow\rangle_p - |\downarrow\rangle_e \otimes |\uparrow\rangle_p\right) \tag{3.55}$$

These states $|j, m_j\rangle$ are actually eigenstates of the total angular momentum operators $\hat{\mathbf{S}}^2$ and \hat{S}_z as defined in Eq. (3.51) with eigenvalues $j(j+1)\hbar^2$ and $m_j\hbar$, respectively, as direct evaluation shows (see also exercises). Thus the structure of the solutions can be seen as a consequence, that the Hamiltonian (3.53) commutes with the total angular momentum (i.e. $[\hat{H}, \hat{S}_i] = 0$ for i = x, y, z, as shown in the exercises). As discussed above, the commutation relations have their origin in spatial symmetry and thus they reflect the fact that the Hamiltonian for the positronium atom has to be invariant under spatial rotations.

Some physical background: The singlet with total spin 0 is called para-positronium and is the ground state. It decays with a mean lifetime of 125 ps into two photons flying in opposite direction of 511 keV each. (This pair of photons is actually used in positron emission tomography). The triplet with spin 1 is called orthopositronium and is an excited state about 0.84 meV above the ground state⁷. Due to its internal symmetry it cannot decay into two photons, and the required three-photon process provides a significantly longer lifetime of 142 ns.⁸

3.4.3 Spin-Orbit Coupling and Fine Structure

Now we consider both the orbital- and spin-degree of freedom of an electron together. (The results obtained here can be easily generalized to the coupling of other kinds of angular momentum.) Thus we have to work in the product space between the spin-1/2 kets and the spatial kets, which is spanned by the basis elements $|\uparrow\rangle \otimes |\mathbf{r}\rangle$, $|\downarrow\rangle \otimes |\mathbf{r}\rangle$, where \mathbf{r} runs over the entire space. The representation of an arbitrary quantum state in this basis is the spinor

$$|\Psi\rangle \to \begin{pmatrix} \Psi_{\uparrow}(\mathbf{r}) \\ \Psi_{\downarrow}(\mathbf{r}) \end{pmatrix}$$
(3.56)

In the following we want to classify the possible eigenstate of angular momentum in this product space.

Eigenstates of total angular momentum

As the spin $\hat{\mathbf{S}}$ and orbital angular momentum $\hat{\mathbf{L}}$ act in different ket spaces we find $[\hat{L}_i, \hat{S}_j] = 0$ for all i, j = x, y, z. Thus the operators $\hat{\mathbf{L}}^2$, \hat{L}_z , $\hat{\mathbf{S}}^2$ and S_z all commute with each other and we can identify a basis, which consists of eigenstates of all these four operators. According to their eigenvalues, these basis elements can be denominated as $|a, l, m_l, s, m_s\rangle_1$, where a is lifting any remaining degeneracies.

System 1: $ a, l, m_l, s, m_s\rangle_1$ are eigenstates of $\hat{\mathbf{L}}^2$, \hat{L}_z , $\hat{\mathbf{S}}^2$, and S_z with	
eigenvalues $l(l+1)\hbar^2$, $m_l\hbar$, $s(s+1)\hbar^2$, and $m_s\hbar$, respectively.	

Here we have $m_l \in \{-l, -l+1, \dots l\}$ and $m_s \in \{-s, -s+1, \dots s\}$. In our case of an electron s = 1/2 is fixed, (but we keep the index in order to be more general)

⁷according to T. Yamazaki, Phys. Rev. Lett. **108**, 253401 (2012)

⁸Lifetimes after A. Badertscher *et al.* Phys. Rev. D **75**, 032004 (2007)

and an example for a spinor representation is

$$|a, l = 2, m_l = 1, s = 1/2, m_s = 1/2 \rangle_1 \to \begin{pmatrix} Y_2^1(\theta, \varphi) f_{a,l}(r) \\ 0 \end{pmatrix}$$

where $f_{a,l}(r)$ is some radial function.

The total angular momentum is the sum of the spin and orbital part $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ and satisfies the general commutation relations for angular momenta as can be easily checked in the exercises. Thus one can construct a basis with common eigenstates of $\hat{\mathbf{J}}^2$ and \hat{J}_z . For the square of the total angular momentum we find

$$\hat{\mathbf{J}}^{2} = \hat{\mathbf{L}}^{2} + \hat{\mathbf{S}}^{2} + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \hat{\mathbf{L}}^{2} + \hat{\mathbf{S}}^{2} + 2\hat{L}_{z}\hat{S}_{z} + \hat{L}_{+}\hat{S}_{-} + \hat{L}_{-}\hat{S}_{+}$$
(3.57)

As $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$ both commute with \hat{L}_z and \hat{S}_z , we obtain the commutation relations

$$[\hat{\mathbf{J}}^2, \hat{L}_z] = 2\sum_n [\hat{L}_n, \hat{L}_z] \hat{S}_n = 2i\hbar(-\hat{L}_y \hat{S}_x + \hat{L}_x \hat{S}_y)$$
(3.58)

$$[\hat{\mathbf{J}}^{2}, \hat{S}_{z}] = 2\sum_{n} \hat{L}_{n} \cdot [\hat{S}_{n}, \hat{S}_{z}] = 2i\hbar(\hat{L}_{y}\hat{S}_{x} - \hat{L}_{x}\hat{S}_{y})$$
(3.59)

Therefore it is not possible to find a common system of eigenstates of $\hat{\mathbf{J}}^2$ and \hat{L}_z or of $\hat{\mathbf{J}}^2$ and \hat{S}_z . Consequently, the states of system 1 cannot be chosen to be eigenstates of $\hat{\mathbf{J}}^2$ as well (except for special cases when l = 0 or s = 0).

However we find:

$$[\hat{\mathbf{J}}^2, \hat{\mathbf{L}}^2] = 2\sum_n [\hat{L}_n, \hat{\mathbf{L}}^2] \hat{S}_n = 0, \qquad [\hat{J}_z, \hat{\mathbf{L}}^2] = 0 \qquad (3.60)$$

$$[\hat{\mathbf{J}}^2, \hat{\mathbf{S}}^2] = 2\sum_n \hat{L}_n[\hat{S}_n, \hat{\mathbf{S}}^2] = 0, \qquad [\hat{J}_z, \hat{\mathbf{S}}^2] = 0 \qquad (3.61)$$

Together with the relation $[\hat{J}_z, \hat{\mathbf{J}}^2] = 0$ we find, that there exists a common system of eigenstates of the operators $\hat{\mathbf{J}}^2, \hat{J}_z, \hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$ namely

System 2:
$$|a, j, m_j, l, s\rangle_2$$
 are common eigenstates of $\hat{\mathbf{J}}^2$, \hat{J}_z , $\hat{\mathbf{L}}^2$, and $\hat{\mathbf{S}}^2$ with eigenvalues $j(j+1)\hbar^2$, $m_j\hbar$, $l(l+1)\hbar^2$, and $s(s+1)\hbar^2$, respectively

As system 1 and system 2 span the same ket space, it must be possible to express the basis states of one system as linear combination of the basis of the other system. The change in bases is given by

$$|j, m_j, l, s\rangle_2 = \sum_{m_l=-l}^{l} \sum_{m_s=-s}^{s} C(j, m_j; m_l, m_s; l, s) |l, m_l, s, m_s\rangle_1$$

where the numbers $C(j, m_j; m_l, m_s; l, s)$ are the Clebsch-Gordan coefficients.⁹ In particular $C(j, m_j; m_l, m_s; l, s) = 0$ holds, if $m_j \neq m_l + m_s$ as $\hat{J}_z = \hat{L}_z + \hat{S}_z$.

Example: Determine the Clebsch-Gordan coefficients of the state $|\Psi\rangle = \left|j = \frac{1}{2}, m_j = \frac{1}{2}, l = 1, s = \frac{1}{2}\right\rangle_2$.

As $m_l + m_s = 1/2$ we have to consider the two states

$$|0\rangle = \left| l = 1, m_l = 0, s = \frac{1}{2}, m_s = \frac{1}{2} \right\rangle_1 \quad |1\rangle = \left| l = 1, m_l = 1, s = \frac{1}{2}, m_s = -\frac{1}{2} \right\rangle_1$$

of system 1 and write $|\Psi\rangle = a_0|0\rangle + a_1|1\rangle$. According to its definition $\hat{\mathbf{J}}^2|\Psi\rangle = \frac{3}{4}\hbar^2|\Psi\rangle$. Using Eqs. (3.57,3.4,3.5) we find

$$\begin{aligned} \frac{3}{4}(a_0|0\rangle + a_1|1\rangle) &= \frac{1}{\hbar^2}(\hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2 + 2\hat{L}_z\hat{S}_z + \hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+)(a_0|0\rangle + a_1|1\rangle) \\ &= a_0\left[\left(2 + \frac{3}{4}\right)|0\rangle + \sqrt{2}|1\rangle\right] + a_1\left[\left(2 + \frac{3}{4} - 1\right)|1\rangle + \sqrt{2}|0\rangle\right] \end{aligned}$$

Comparing the coefficients of $|0\rangle$ and $|1\rangle$ provides

$$\frac{3}{4}a_0 = \left(2 + \frac{3}{4}\right)a_0 + \sqrt{2}a_1$$
 and $\frac{3}{4}a_1 = \left(1 + \frac{3}{4}\right)a_1 + \sqrt{2}a_0$

with the solution $a_1 = -\sqrt{2}a_0$. Normalizing $|a_0|^2 + |a_1|^2 = 1$ provides

$$a_0 = C(j = 1/2, m_j = 1/2; m_l = 0, m_s = 1/2; l = 1, s = 1) = -\frac{1}{\sqrt{3}}$$
$$a_1 = C(j = 1/2, m_j = 1/2; m_l = 1, m_s = -1/2; l = 1, s = 1) = \sqrt{\frac{2}{3}}$$

In spinor representation we can write

$$\left| j = \frac{1}{2}, m_j = \frac{1}{2}, l = 1, s = \frac{1}{2} \right\rangle_2 \to \frac{1}{\sqrt{3}} \begin{pmatrix} -Y_1^0(\theta, \varphi) \\ \sqrt{2}Y_1^1(\theta, \varphi) \end{pmatrix}$$

⁹See, e.g., http://pdg.lbl.gov/2011/reviews/rpp2011-rev-clebsch-gordan-coefs.pdf

Fine structure of the hydrogen atom

For the hydrogen atom the main ingredient of the Hamiltonian is the Coulomb potential of the proton, which does not depend on spin. Thus the corresponding Hamilton operator is diagonal in spin space and the energy eigenvalues $13.6 \text{ eV}/n^2$ only depend on the principal quantum number n together with the restriction l < n. In this case we can use either system 1 or system 2 for a classification of the states.

As both spin and orbital angular momentum are related to a magnetic moment, the interaction between these moments provides the *Spin-orbit-interaction*

$$\hat{H}_{\rm SO} = f(r)\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2}f(r)\left(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2\right)$$
(3.62)

A relativistic calculation (e.g., Bransden and Joachain, *Quantum Mechanics*, chapter 15.6) provides for a central potential:

$$f(r) = \frac{1}{2m_e^2 c^2} \frac{1}{r} \frac{\partial V}{\partial r}$$

Together with Eqs. (3.58, 3.59) it follows

$$[\hat{H}_{\mathrm{SO}}, \hat{L}_z] = \mathrm{i}f(r)\hbar(-\hat{L}_y\hat{S}_x + \hat{L}_x\hat{S}_y) \quad \text{and} \quad [\hat{H}_{\mathrm{SO}}, \hat{S}_z] = \mathrm{i}f(r)\hbar(\hat{L}_y\hat{S}_x - \hat{L}_x\hat{S}_y)$$

Thus, there is no common set of eigenstates of \hat{H}_{SO} and \hat{L}_z or \hat{S}_z , and neither m_l nor m_s are good quantum numbers to describe the energy levels of the hydrogen atom if spin-orbit interaction is considered, i.e., our system 1 is of no use. In contrast we find with Eqs. (3.60,3.61):

$$[\hat{H}_{\rm SO}, \hat{\mathbf{J}}^2] = 0, \quad [\hat{H}_{\rm SO}, \hat{J}_z] = 0, \quad [\hat{H}_{\rm SO}, \hat{\mathbf{L}}^2] = 0, \text{ and } \quad [\hat{H}_{\rm SO}, \hat{\mathbf{S}}^2] = 0$$

Thus there exists a common system of eigenstates of the operators \hat{H}_{SO} , $\hat{\mathbf{J}}^2$, \hat{J}_z , $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$. We conclude that system 2 with the quantum numbers j, m_j , l and s is appropriate to describe the energy levels of the hydrogen atom if spin-orbit interaction is considered. Due to symmetry, these provide multiplets, with respect to the index m_j . Thus the levels can be classified by n, l and j in the form nl_j , called spectroscopic notation, where l is replaced by the letters s,p,d,f for l = 0, 1, 2, 3, respectively.

How are the energy levels changed by the spin-orbit interaction?

78

ground state n = 1; l = 0; s = 1/2: This only allows j = 1/2. As j(j + 1) - l(l + 1) - s(s + 1) = 0 in Eq. (3.62) the spin orbit interaction vanishes

i(i + 1) - s(s + 1) = 0 in Eq. (5.02) the spin orbit interaction van

 \rightarrow No change in energy for ground state $1 \mathrm{s}_{1/2}$

first exited state n = 2; l = 0, 1; s = 1/2. Possible states in system 2 are:

- $|j = \frac{1}{2}, m_j = \pm \frac{1}{2}, l = 0, s = \frac{1}{2}\rangle_2$: provides j(j+1) l(l+1) s(s+1) = 0 \rightarrow No change in energy for $2s_{1/2}$
- $|j = \frac{1}{2}, m_j = \pm \frac{1}{2}, l = 1, s = \frac{1}{2}\rangle_2$: Then we find j(j+1) l(l+1) s(s+1) = -2

 \rightarrow reduction in energy for $2 p_{1/2}$

• $|j = \frac{3}{2}, m_j = \pm \frac{1}{2}, \pm \frac{3}{2}, l = 1, s = \frac{1}{2}\rangle_2$: Then we find j(j+1) - l(l+1) - s(s+1) = 1

 \rightarrow increase in energy for $2p_{3/2}$

Spin-orbit interaction lifts the degeneracy between states with different j and l of the hydrogen atom, which is called *fine structure*

In addition, further relativistic terms and the Lamb shift have to be considered for a quantitative description. However the classification of the states remains valid, as it is a consequence of symmetry¹⁰. We could make rather general statements and avoided the effort of matrix diagonalization as we implied the correct symmetry. Finally, note that the energy shifts by the fine structure are of the order of 41μ eV (shift between $2p_{1/2}$ and $2p_{3/2}$ ¹¹) and thus significantly smaller than the energy difference between the n = 1 and n = 2 state of approximately 10 eV. The hyperfine-structure due to the coupling to the magnetic moment of the proton is even smaller (the splitting between the singlet and the triplet in the ground states is 6 μ eV¹². This is much smaller than for the case of positronium (Sec. 3.4.2) as the magnetic moment of the proton is much smaller than the one of the positron due to the substantially higher mass.

¹⁰The ordering of levels is also preserved, albeit only a little difference between $2s_{1/2}$ and $2p_{1/2}$, called Lamb shift, remains. See, e.g., the textbook of Bransden and Joachain

¹¹According to E.W. Hagley and F.M. Pipkin, Phys. Rev. Lett. **72**, 1172 (1994)

 $^{^{12}}$ according to D.J. Griffiths, Am. J. Phys **50**, 698 (1982), where a simple quantitative calculation is performed

CHAPTER 3. ANGULAR MOMENTUM

Chapter 4

Magnetic Fields

Up to now we considered quantum systems which correspond to classical systems with a mechanical potential $V(\mathbf{r})$ as well as the spin, where no classical analog exists. Now we focus on electromagnetic fields, where the Lorentz force

$$\mathbf{F} = q\mathbf{v} \times \mathbf{B} + q\mathbf{E} \tag{4.1}$$

on a particle with charge q due to the electric field $\mathbf{E}(\mathbf{r}, t)$ and the magnetic field $\mathbf{B}(\mathbf{r}, t)$ is not the gradient of any potential $V(\mathbf{r})$.

4.1 Hamilton Operator in an Electromagnetic Field

4.1.1 The electromagnetic potentials

The homogeneous Maxwell equations (the equations, which do not contain charges or currents) read

$$\nabla\cdot\mathbf{B}(\mathbf{r},t)=0 \quad \text{and} \quad \nabla\times\mathbf{E}(\mathbf{r},t)=-\frac{\partial}{\partial t}\mathbf{B}(\mathbf{r},t)$$

The first one implies the existence of a field $\mathbf{A}(\mathbf{r},t)$ (called vector potential), with $\mathbf{B}(\mathbf{r},t) = \nabla \times \mathbf{A}(\mathbf{r},t)$. Inserting this into the second equation provides $\nabla \times (\mathbf{E} + \partial \mathbf{A}/\partial t) = 0$. This in turn implies the existence of function $\phi(\mathbf{r},t)$ (called scalar potential) with $\mathbf{E} + \partial \mathbf{A}/\partial t = -\nabla \phi(\mathbf{r},t)$. In summary, the electric and magnetic field can be expressed by potentials as

$$\mathbf{E}(\mathbf{r},t) = -\nabla\phi(\mathbf{r},t) - \frac{\partial\mathbf{A}(\mathbf{r},t)}{\partial t} \qquad \mathbf{B}(\mathbf{r},t) = \nabla \times \mathbf{A}(\mathbf{r},t)$$
(4.2)

which satisfies the two homogeneous Maxwell equations. This generalizes the (possibly better known) stationary case with time-independent fields and potentials, where $\mathbf{E}(\mathbf{r}) = -\nabla \phi(\mathbf{r})$ and $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$.

For example, the electromagnetic wave

$$\mathbf{E}(\mathbf{r},t) = E_0 \mathbf{e}_x \cos(kz - \omega t) \qquad \mathbf{B}(\mathbf{r},t) = \frac{kE_0}{\omega} \mathbf{e}_y \cos(kz - \omega t)$$

can be expressed by the potentials

$$\mathbf{A}(\mathbf{r},t) = \frac{1}{\omega} E_0 \mathbf{e}_x \sin(kz - \omega t) \qquad \phi(\mathbf{r},t) = 0$$

Note that the potentials are not unique as the substitution

$$\mathbf{A}'(\mathbf{r},t) = \mathbf{A}(\mathbf{r},t) + \nabla F(\mathbf{r},t) \qquad \phi'(\mathbf{r},t) = \phi(\mathbf{r},t) - \frac{\partial}{\partial t}F(\mathbf{r},t)$$
(4.3)

provides identical fields for arbitrary scalar functions $F(\mathbf{r}, t)$, which is called a gauge transformation. This provides the freedom to specify $\nabla \cdot \mathbf{A}(\mathbf{r}, t)$. Common choices are $\nabla \cdot \mathbf{A}(\mathbf{r}, t) = 0$ (Coulomb gauge) and $\nabla \cdot \mathbf{A}(\mathbf{r}, t) = -c^{-2}\partial\phi(\mathbf{r}, t)/\partial t$ (Lorenz gauge).

4.1.2 Main result

While the potentials $\mathbf{A}(\mathbf{r}, t)$, $\phi(\mathbf{r}, t)$ are useful (but not necessary) in classical electrodynamics, they become of central importance in the formulation of the quantum theory for particles interacting with electromagnetic fields. The main concept is summarized as follows:

The Hamilton operator for particles with mass m and charge q reads

$$\hat{H} = \frac{(\hat{\mathbf{p}} - q\mathbf{A}(\hat{\mathbf{r}}, t))^2}{2m} + q\phi(\hat{\mathbf{r}}, t)$$
(4.4)

where the operators $\hat{\mathbf{p}}$ and $\hat{\mathbf{r}}$ satisfy the canonical commutation relations

$$[\hat{p}_i, \hat{r}_j] = \frac{h}{i} \delta_{ij} \qquad [\hat{p}_i, \hat{p}_j] = 0 \qquad [\hat{r}_i, \hat{r}_j] = 0 \tag{4.5}$$

In spatial representation, the *(canonical) momentum* operator $\hat{\mathbf{p}}$ becomes $\frac{\hbar}{i}\nabla$ as usual. However it differs from the *kinetic momentum*

$$\hat{\mathbf{p}}^{\text{kin}} = \hat{\mathbf{p}} - q\mathbf{A}(\hat{\mathbf{r}}, t)$$
 providing the average velocity $\langle \mathbf{v} \rangle = \frac{\langle \Psi | \hat{\mathbf{p}}^{\text{kin}} | \Psi \rangle}{m}$ (4.6)

This structure of the Hamilton operator can be deduced in the context of analytical mechanics by considering the classical Hamilton function¹. As a less formal alternative, we show in Sec. 4.1.3, that the Hamiltonian provides the same equations of motion for the expectation value of the position operator as the classical theory and thus makes sense.

In this context it is important to notice, that the components of $\hat{\mathbf{p}}^{kin}$ do not satisfy the canonical commutation relations. Instead we find the important relation

$$\begin{aligned} [\hat{p}_i^{\text{kin}}, \hat{p}_j^{\text{kin}}] &= [\hat{p}_i - qA_i(\hat{\mathbf{r}}, t), \hat{p}_j - qA_j(\hat{\mathbf{r}}, t)] = -q[\hat{p}_i, A_j(\hat{\mathbf{r}}, t)] - q[A_i(\hat{\mathbf{r}}, t), \hat{p}_j] \\ &= i\hbar q \left(\frac{\partial A_j(\hat{\mathbf{r}}, t)}{\partial r_i} - \frac{\partial A_i(\hat{\mathbf{r}}, t)}{\partial r_j}\right) = i\hbar q\epsilon_{ijk}B_k(\hat{\mathbf{r}}, t) \end{aligned}$$
(4.7)

where we used the relation

$$[\hat{p}_j, f(\hat{\mathbf{r}})] = \frac{\hbar}{\mathrm{i}} \frac{\partial f(\hat{\mathbf{r}})}{\partial r_j} \tag{4.8}$$

and $\nabla \times \mathbf{A} = \mathbf{B}$ from Eq. (4.2), where ϵ_{ijk} is the Levi-Civita tensor.

¹See, http://www.teorfys.lu.se/staff/Andreas.Wacker/Scripts/quantMagnetField. pdf for a short outline.

4.1.3 Justification of the Hamiltonian^{*}

In order to justify the choice (4.4) for the Hamiltonian in the presence of an electromagnetic field we consider the time evolution of the average position.

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\Psi|\hat{\mathbf{r}}|\Psi\rangle = \frac{\mathrm{i}}{\hbar}\langle\Psi|\left[\left(\frac{(\hat{\mathbf{p}} - q\mathbf{A}(\hat{\mathbf{r}}, t))^2}{2m} + q\phi(\hat{\mathbf{r}}, t)\right), \hat{\mathbf{r}}\right]|\Psi\rangle = \langle\Psi|\frac{\hat{\mathbf{p}} - q\mathbf{A}(\hat{\mathbf{r}}, t)}{m}|\Psi\rangle$$

in agreement with Eq. (4.6).

Now we evaluate the expectation value for the acceleration times the particle mass, which should correspond to the classical Lorentz force (4.1).

$$\begin{split} m\frac{\mathrm{d}^{2}}{\mathrm{d}t^{2}}\langle\Psi|\hat{\mathbf{r}}|\Psi\rangle &= \frac{\mathrm{d}}{\mathrm{d}t}\langle\Psi|\hat{\mathbf{p}}^{\mathrm{kin}}|\Psi\rangle = \frac{\mathrm{i}}{\hbar}\langle\Psi|[\hat{H},\hat{\mathbf{p}}^{\mathrm{kin}}]|\Psi\rangle + \langle\Psi|\left(\frac{\partial}{\partial t}\hat{\mathbf{p}}^{\mathrm{kin}}\right)|\Psi\rangle \\ &= \underbrace{\frac{\mathrm{i}}{\hbar}\langle\Psi|\left[\frac{(\hat{\mathbf{p}}^{\mathrm{kin}})^{2}}{2m},\hat{\mathbf{p}}^{\mathrm{kin}}\right]|\Psi\rangle}_{\mathrm{Term \ II}} + \underbrace{\frac{\mathrm{i}}{\hbar}\langle\Psi|\left[q\phi(\hat{\mathbf{r}},t),\hat{\mathbf{p}}^{\mathrm{kin}}\right]|\Psi\rangle}_{\mathrm{Term \ II}} \underbrace{-q\langle\Psi|\frac{\partial}{\partial t}\mathbf{A}(\hat{\mathbf{r}},t)|\Psi\rangle}_{\mathrm{Term \ III}} \end{split}$$

The commutator in Term 2 becomes just $i\hbar q \frac{\partial \phi(\hat{\mathbf{r}},t)}{\partial \mathbf{r}}$ using Eq. (??). Comparing with Eq. (4.2) we identify

Terms II+III =
$$\langle \Psi | q \mathbf{E}(\hat{\mathbf{r}}, t) | \Psi \rangle$$

which is just the electric field part of the Lorentz force (4.1).

In term I we consider

$$\begin{bmatrix} (\hat{p}_i^{\mathrm{kin}})^2, \hat{p}_j^{\mathrm{kin}} \mathbf{e}_j \end{bmatrix} = \left(\hat{p}_i^{\mathrm{kin}} [\hat{p}_i^{\mathrm{kin}}, \hat{p}_j^{\mathrm{kin}}] + [\hat{p}_i^{\mathrm{kin}}, \hat{p}_j^{\mathrm{kin}}] \hat{p}_i^{\mathrm{kin}} \right) \mathbf{e}_j$$
$$= \mathrm{i}\hbar q \epsilon_{ijk} \left(\hat{p}_i^{\mathrm{kin}} B_k(\hat{\mathbf{r}}, t) + B_k(\hat{\mathbf{r}}, t) \hat{p}_i^{\mathrm{kin}} \right) \mathbf{e}_j$$

where Eq. (4.7) was used. This can be written as a cross product we obtain

Term I =
$$q\langle \Psi | \left(\frac{\hat{\mathbf{p}}^{\text{kin}}}{2m} \times \mathbf{B}(\hat{\mathbf{r}}, t) - \mathbf{B}(\hat{\mathbf{r}}, t) \times \frac{\hat{\mathbf{p}}^{\text{kin}}}{2m} \right) | \Psi \rangle$$

which is a symmetrized version of the magnetic field part of the Lorentz force (4.1). Together we find

$$m\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle\Psi|\hat{\mathbf{r}}|\Psi\rangle = q\langle\Psi|\left(\frac{\hat{\mathbf{p}}^{\mathrm{kin}}}{2m}\times\mathbf{B}(\hat{\mathbf{r}},t) - \mathbf{B}(\hat{\mathbf{r}},t)\times\frac{\hat{\mathbf{p}}^{\mathrm{kin}}}{2m}\right)|\Psi\rangle + q\langle\Psi|\mathbf{E}(\hat{\mathbf{r}},t)|\Psi\rangle$$

which corresponds to the expectation value of the classical equation of motion.² This general correspondence between classical and quantum physics is called *Ehren*-fest theorem.

4.2 Zeeman Effect

A constant magnetic field \mathbf{B} can be described via the vector potential

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r} \tag{4.9}$$

Including a static electric potential ϕ the Hamiltonian (4.4) reads

$$\hat{H} = \frac{(\hat{\mathbf{p}}^2 - q\mathbf{A}(\hat{\mathbf{r}}) \cdot \hat{\mathbf{p}} - q\hat{\mathbf{p}} \cdot \mathbf{A}(\hat{\mathbf{r}}) + q^2\mathbf{A}^2(\hat{\mathbf{r}})}{2m} + q\phi(\hat{\mathbf{r}})$$

The choice (4.9) of the vector potential, satisfies $\nabla \cdot \mathbf{A}(\mathbf{r}) = 0$ (also called Coulomb gauge). Then we find with help of Eq. (4.8)

$$\hat{\mathbf{p}} \cdot \mathbf{A}(\hat{\mathbf{r}}) - \mathbf{A}(\hat{\mathbf{r}}) \cdot \hat{\mathbf{p}} = \sum_{j} [\hat{p}_{j}, A_{j}(\hat{\mathbf{r}})] = \frac{\hbar}{\mathrm{i}} \sum_{j} \frac{\partial}{\partial r_{j}} A_{j}(\hat{\mathbf{r}}) = \frac{\hbar}{\mathrm{i}} \nabla \cdot \mathbf{A}(\hat{\mathbf{r}}) = 0$$

Thus we can write

$$-q\mathbf{A}(\hat{\mathbf{r}})\cdot\hat{\mathbf{p}}-q\hat{\mathbf{p}}\cdot\mathbf{A}(\hat{\mathbf{r}})=-2q\mathbf{A}(\hat{\mathbf{r}})\cdot\hat{\mathbf{p}}=-q(\mathbf{B}\times\hat{\mathbf{r}})\cdot\hat{\mathbf{p}}=-(\hat{\mathbf{r}}\times\hat{\mathbf{p}})\cdot\mathbf{B}=-\hat{\mathbf{L}}\cdot\mathbf{B}$$

Furthermore we have

$$\begin{aligned} \mathbf{A}^{2}(\hat{\mathbf{r}}) =& \frac{1}{4} (\mathbf{B} \times \hat{\mathbf{r}}) \cdot (\mathbf{B} \times \hat{\mathbf{r}}) = \frac{1}{4} \left[\hat{\mathbf{r}} \times (\mathbf{B} \times \hat{\mathbf{r}}) \right] \cdot \mathbf{B} \\ =& \frac{1}{4} \left[\hat{\mathbf{r}}^{2} \mathbf{B} - (\mathbf{B} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} \right] \cdot \mathbf{B} = \frac{1}{4} \mathbf{B}^{2} \hat{\mathbf{r}}_{\perp}^{2} \end{aligned}$$

where $\hat{\mathbf{r}}_{\perp}$ is the component of $\hat{\mathbf{r}}$ which is perpendicular to **B**.

In summary we find the Hamiltonian for a charged particle in a constant magnetic field and a static electric potential:

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + q\phi(\hat{\mathbf{r}}) - \frac{q}{2m}\mathbf{B}\cdot\hat{\mathbf{L}} + \frac{q^2\mathbf{B}^2}{8m}\hat{\mathbf{r}}_{\perp}^2$$
(4.10)

²Note however, that on the right-hand side, the expectation value is taken over the fields and not directly over the spatial operator. Thus these does not provide a closed system of equations, in contrast to the classical case!

For atoms the last term is usually negligible. For the typical atomic length scale $\hat{\mathbf{r}}_{\perp}^2 \sim 1 \mathring{A}^2$, we obtain about $0.2 \text{neV} \times (B/\text{T})^2$, which is very small. (Note that magnetic fields of more than a few Tesla require substantial experimental effort.)

Lets now consider the hydrogen atom and $\phi(\hat{\mathbf{r}})$ is the Coulomb potential of the proton. Then the kets $|n, l, m_l\rangle$ are the well-known eigenstates of $\frac{\hat{\mathbf{p}}^2}{2m} + q\phi(\hat{\mathbf{r}})$ with energy E_n . Adding a magnetic field in z-direction provides the additional term $\frac{e}{2m_e}B\cdot\hat{L}_z$ which splits each multiplet with fixed l into 2l+1 lines with energy shifts $\frac{e\hbar}{2m_e}m_lB$. Such a splitting of degenerate states in a multiplet is called Zeeman effect. The Bohr magneton

$$\mu_B = \frac{e\hbar}{2m_e} = 57.88\dots\mu eV/T \tag{4.11}$$

provides the magnitude of the splitting between two lines.

Combining with the Hamiltonian for the electron spin $H = g_e \frac{e}{2m_e} \boldsymbol{B} \cdot \hat{\boldsymbol{S}}$, the influence of a constant magnetic field (in z-direction) on a bound electron is given by the Hamiltonian

$$\hat{H}_{e-B} = \frac{e}{2m_e} B\left(\hat{L}_z + g_e \hat{S}_z\right)$$

Is this operator compatible with the common quantum numbers? We find that \hat{H}_{e-B} commutes with \hat{L}_z , \hat{S}_z , as well as their sum \hat{J}_z . Furthermore $[\hat{H}_{e-B}, \hat{\mathbf{L}}^2] = 0$ and $[\hat{H}_{e-B}, \hat{\mathbf{S}}^2] = 0$. Thus there is a common system of quantum number $|l, m_l, s, m_s\rangle$ with the operators \hat{L}_z , \hat{S}_z , $\hat{\mathbf{L}}^2$, and $\hat{\mathbf{S}}^2$. This provides the splitting

$$|n = 2, l = 1, m_l, s = 1/2, m_s \rangle_1$$
 splits as $\mu_B B(m_L + g_e m_s)$

On the other hand we learned that to describe spin-orbit interaction one has to use the basis of total angular momentum $|j, m, l, s\rangle$. However, we find that in the presence of a magnetic field the commutator

$$\left[\frac{e}{2m_e}B(\hat{L}_z + g_e\hat{S}_z), \hat{\mathbf{J}}^2\right] = \frac{e}{2m_e}B(g_e - 1)[\hat{S}_z, \hat{\mathbf{J}}^2] = \mathrm{i}\hbar \frac{eB(g_e - 1)}{m_e}(\hat{L}_x\hat{S}_y - \hat{L}_y\hat{S}_x)$$

is finite, where the relation $[\hat{L}_z + \hat{S}_z, \hat{\mathbf{J}}^2] = 0$ and $[\hat{S}_z, \hat{\mathbf{J}}^2] = 2i\hbar(\hat{L}_x\hat{S}_y - \hat{L}_y\hat{S}_x)$ was used. Thus there are no common eigenstates of $\hat{\mathbf{J}}^2$ and the Hamiltonian in the presence of a magnetic field and system 2 cannot be entirely right.

The energy of the spin-orbit interaction is comparable with $\mu_B B$ for magnetic fields of the order of 1 Tesla. Thus for much larger fields, we may neglect the



Figure 4.1: Results of a complete diagonalization of the LS-coupling and the external field term $\hat{H} = \frac{2\alpha}{\hbar^2} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} + \frac{\mu_B B}{\hbar} \left(\hat{L}_z + 2\hat{S}_z \right)$ for the six states of the 2p level. For B = 0 we recover the fine structure, which splits in the magnetic field. For $\mu B \gg \alpha$, the lines follow approximatively $\mu_B B(m_l + 2m_S) + 2\alpha m_l m_s$. Since m_j is a good quantum number in both systems 1 and 2, states with different m_j -values do not interact (and may thus cross each other). In contrast, the two states with $m_j = 1/2$ (and similarly for $m_j = -1/2$) couple to each other and thus neither j nor m_l, m_s are good quantum numbers for $B \neq 0$. For the hydrogen atom, we have $\alpha \approx 14\mu$ eV and $\alpha/\mu_B \approx 0.24$ Tesla.

spin-orbit interaction and consider the Zeeman splitting within system 1. In the opposite case of much weaker field, one can find the splitting of the fine-structure levels according to m_j with an effective g-factor as described in the chapter on perturbation theory. This is illustrated in Fig. (4.1).

4.3 Landau Levels

Having considered the bound state before, we now focus on a free electron in a constant magnetic field as described by Eq. (4.10). If the magnetic field points in z-direction we find

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} - \frac{q}{2m}B\hat{L}_z + \frac{q^2B^2}{8m}(\hat{x}^2 + \hat{y}^2)$$
(4.12)

This Hamiltonian is rotational invariant with respect to the z- axis. Thus $[\hat{H}, \hat{L}_z] = 0$. Similarly $[\hat{H}, \hat{p}_z] = 0$ holds. Thus we have a joint set of eigenstates of \hat{H}, \hat{p}_z , and \hat{L}_z .

At first we can separate the z direction, where the eigenstates are plane waves e^{ikz} in spatial representation with energy $E(k) = \hbar^2 k^2/2m$. We are left with a two-dimensional problem

$$\hat{H} = \frac{\hat{p}_x^2 + \hat{p}_y^2}{2m} - \frac{q}{2m}B\hat{L}_z + \frac{q^2B^2}{8m}(\hat{x}^2 + \hat{y}^2)$$

With $\omega = qB/(2m)$ this provides

$$\hat{H} = \underbrace{\frac{\hat{p}_x^2 + \hat{p}_y^2}{2m} + \frac{1}{2}m\omega^2(\hat{x}^2 + \hat{y}^2)}_{\hat{H}_{\text{osc}}} - \omega\hat{L}_z$$

Now \hat{H}_{osc} is just the two-dimensional isotropic oscillator which can be immediately solved, yielding energy levels $E_N = \hbar \omega (N+1)$ where N = 0, 1, 2, ... and there are N + 1 states for each level N.

As $[\hat{H}_{\text{osc}}, \hat{L}_z] = 0$ these states can be chosen as eigenstates of \hat{L}_z . In spatial representation with polar coordinates r, φ we find $\hat{L}_z^{\text{SR}} = \frac{\hbar}{i} \frac{\partial}{\partial \varphi}$ with eigenstates $e^{im\varphi}$ and eigenvalues $m\hbar$, which fully agrees with the three dimensional case.³ Then one finds the

Proposition: The eigenstates of the two-dimensional harmonic oscillator \hat{H}_{osc} with energy $E_N = \hbar \omega (N+1)$ can be classified as the (N+1) states $|N, m_N\rangle$ with $m_N = -N, 2 - N, \ldots N$, where $\hat{L}_z |N, m_N\rangle = m_N \hbar |N, m_N\rangle$.

³Note that \hat{H}_{osc} does not commute with \hat{L}_x and \hat{L}_y . Thus we do note find the multiplets $m = -l, -l+1, \ldots l$ as characteristic for systems which are rotational invariant in all three spatial directions.



Figure 4.2: Sketch for the origin of Landau levels. In the left panel, the eigenstates of $\frac{\hat{p}_x^2 + \hat{p}_y^2}{2m} + \frac{1}{2}m\omega^2(\hat{x}^2 + \hat{y}^2)$ re shown and classified according to the quantum number m_N . In the right panel the additional term $-\omega \hat{L}_z$ is taking into account, where $\omega = qB/(2m)$.

which is proven in Sec. 4.3.1 and is depicted in the left panel of Fig. 4.2. Now the term $-\omega \hat{L}_z$ provides the additional energy $-\hbar\omega m$ and thus the total energy of the state $|N, m_N\rangle$ is

$$E(N, m_N) = E_N - \hbar \omega m_N = \hbar \omega (N - m_N + 1)$$
(4.13)

as shown in the right panel of Fig. 4.2. For each N the maximal possible m_N provides $E(N, N) = \hbar \omega$. The next largest m_N provides $E(N, N - 2) = 3\hbar \omega$ and so on. We find that all these levels have an infinite degeneracy. These levels are called *Landau levels*.

The energy of the Landau levels is given by $\hbar\omega(2n+1)$ or

$$E_{\text{Landau}} = \hbar\omega_c \left(n + \frac{1}{2}\right)$$

where the cyclotron frequency $\omega_c = eB/m$ corresponds to the frequency with which the classical electrons spiral in a constant magnetic field.

4.3.1 Determining the possible m-values of the states $|N, m\rangle$

Here we want to proof the proposition on page 88. Using the standard definitions

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \quad a_x = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}_x, \quad \text{and} \quad a_y = \sqrt{\frac{m\omega}{2\hbar}}\hat{y} + i\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}_y$$

we can directly identify

$$\hat{L}_z = i\hbar(a_y^{\dagger}a_x - a_x^{\dagger}a_y) \tag{4.14}$$

and calculate the commutator relations

$$[\hat{L}_z, a_x^{\dagger}] = i\hbar a_y^{\dagger} \quad \text{and} \quad [\hat{L}_z, a_y^{\dagger}] = -i\hbar a_x^{\dagger} \tag{4.15}$$

With these tools at hand we proof the proposition by induction in N:

For N = 0 the ground state of the harmonic oscillator satisfies $a_x|0,0\rangle = 0$ and $a_y|0,0\rangle = 0$. Thus we find from Eq. (4.14) $\hat{L}_z|0,0\rangle = 0$ and this state is indeed an eigenstate of \hat{L}_z with eigenvalues $m_0 = 0$.

Assume the proposition is valid for a given $N \ge 0$. Then we consider the state

$$|\Psi\rangle = \frac{1}{\sqrt{2}} (a_x^{\dagger} - \mathrm{i} a_y^{\dagger}) |N, m_N\rangle$$

and find

$$\hat{H}|\Psi\rangle = \hbar\omega (a_x^{\dagger}a_x + a_y^{\dagger}a_y + 1)\frac{1}{\sqrt{2}}(a_x^{\dagger} - \mathrm{i}a_y^{\dagger})|N, m_N\rangle = \dots = (N+2)\hbar\omega|\Psi\rangle$$
$$\hat{L}_z|\Psi\rangle = \hat{L}_z\frac{1}{\sqrt{2}}(a_x^{\dagger} - \mathrm{i}a_y^{\dagger})|N, m_N\rangle = \dots = (m_N - 1)\hbar|\Psi\rangle$$

where the commutation rules for the creation/annihilation operators and Eq. 4.15 are applied in the explicit calculation. Thus the state $|\Psi\rangle$ can be classified as $|N+1, m_N - 1\rangle$. Similarly the state $|\Psi\rangle = \frac{1}{\sqrt{2}}(a_x^{\dagger} + ia_y^{\dagger})|N, m_N\rangle$ can be classified as $|N+1, m_N + 1\rangle$. Considering the definition of m_N this procedure constructs states $|N+1, m_{N+1}\rangle$ with $m_{N+1} = -(N+1), -(N+1) + 2, \dots (N+1)$. As the dimension of the subspace of the operator \hat{H} with eigenvalue $(N+1)\hbar\omega$ is just N+1, only N+1 states can be linearly independent, i.e. those with different m. Thus the states $\frac{1}{\sqrt{2}}(a_x^{\dagger} - ia_y^{\dagger})|N, m_N\rangle$ and $\frac{1}{\sqrt{2}}(a_x^{\dagger} + ia_y^{\dagger})|N, m_N - 2\rangle$ may only differ by a phase factor.

Thus the proposition is shown for N + 1 and the proof by induction is closed.

Chapter 5

PERTURBATION THEORY

Only very few physical systems (such as the harmonic oscillator or the hydrogen atom, e.g.) can be solved exactly by analytical methods. Thus one requires approximate solutions of a known Hamiltonian. Even worse, for many systems the forces are not known precisely so one has to "guess" some rough Hamiltonian. Other systems have such a complex structure that it is impossible to take all interactions into account. In this chapter we will first concentrate on approximation methods to calculate eigenvalues and eigenstates to the Hamiltonian. Later we will shift focus and consider time-dependent effects.

In most situations it is reasonable to split the Hamilton operator into a known part \hat{H}_0 (typically time-independent), where one has sufficient knowledge about the eigenstates and their energies (either by calculations or by symmetry arguments), and a *perturbation* term $\hat{V}(t)$

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t).$$
 (5.1)

The eigenstates $|a^0\rangle$ of \hat{H}_0 satisfy

$$\hat{H}_0|a^0\rangle = E_a^0|a^0\rangle \tag{5.2}$$

and form a complete ON basis of the ket space.

5.1 Stationary Perturbation Theory

Let \hat{V} be independent of time. Here we are looking for the exact eigenstates of

$$(\hat{H}_0 + \lambda \hat{V})|a\rangle = E_a|a\rangle.$$
(5.3)

The real parameter λ is included here, which allows to change the magnitude of the perturbation gradually. In the final result, $\lambda = 1$ has to be used. The energies E_a and eigenstates $|a\rangle$ can be expanded in the parameter λ as

$$E_a = E_a^0 + \lambda E_a^1 + \lambda^2 E_a^2 + \dots \qquad |a\rangle = |a^0\rangle + \lambda |a^1\rangle + \lambda^2 |a^2\rangle + \dots \qquad (5.4)$$

which is called *Rayleigh-Schrödinger perturbation series*¹. Here the upper indices label the order on the perturbation series, i.e. E_a^1 denotes the change in energy of the state $|a^0\rangle$ in the first order of the parameter λ . The eigenstates are only defined up to a complex factor. In order to uniquely define the state $|a\rangle$, we impose the normalization $\langle a|a\rangle = 1$ and choose the phase such that $\langle a^0|a\rangle$ is a real positive number for all $\lambda \in \mathbb{R}$. The latter condition provides

$$\langle a^0 | a^n \rangle \in \mathbb{R}$$

and the normalization provides with (5.4)

$$1 = \underbrace{\langle a^0 | a^0 \rangle}_{=1} + \underbrace{\lambda \langle a^0 | a^1 \rangle + \lambda \langle a^1 | a^0 \rangle}_{=2\lambda \operatorname{Re}\{\langle a^0 | a^1 \rangle\}} + \mathcal{O}\{\lambda^2\}$$

Thus $\langle a^0 | a^1 \rangle \in \mathbb{R}$ results in

$$\langle a^0 | a^1 \rangle = 0 \tag{5.5}$$

Inserting the expansion (5.4) into Eq. (5.3) provides:

$$\begin{pmatrix} \hat{H}_0 + \lambda \hat{V} \end{pmatrix} (|a^0\rangle + \lambda |a^1\rangle + \lambda^2 |a^2\rangle + \dots)$$

= $(E_a^0 + \lambda E_a^1 + \lambda^2 E_a^2 + \dots) (|a^0\rangle + \lambda |a^1\rangle + \lambda^2 |a^2\rangle + \dots)$

¹Note that there are many cases, where this expansion does not converge. A prominent example is the one-dimensional harmonic oscillator \hat{H}_0 with $\hat{V}(x) = \alpha \hat{x}^4$ for $\alpha > 0$. Nevertheless the lowest order terms in λ provide typically reasonable approximations.

Sorting the orders in λ^i , one obtains

$$\mathcal{O}(\lambda^{0}) \qquad \qquad \hat{H}_{0}|a^{0}\rangle = E_{a}^{0}|a^{0}\rangle \\ \mathcal{O}(\lambda) \qquad \qquad \hat{H}_{0}|a^{1}\rangle + \hat{V}|a^{0}\rangle = E_{a}^{0}|a^{1}\rangle + E_{a}^{1}|a^{0}\rangle$$
(5.6)

$$\mathcal{O}(\lambda^2) \qquad \hat{H}_0|a^2\rangle + \hat{V}|a^1\rangle = E_a^0|a^2\rangle + E_a^1|a^1\rangle + E_a^2|a^0\rangle \qquad (5.7)$$

Multiplying Eq. (5.6) with $\langle b^0 |$ provides

$$\langle b^0 | \hat{V} | a^0 \rangle = (E_a^0 - E_b^0) \langle b^0 | a^1 \rangle + E_a^1 \delta_{a,b}$$
 (5.8)

Now two different cases have to be considered separately.

5.1.1 Non-degenerate case

Let E_a^0 be an eigenvalue of \hat{H}_0 , which has only one corresponding eigenstate. This means $E_b^0 \neq E_a^0$ for all states $b \neq a$. Such a state $|a^0\rangle$ is called non-degenerate. Then Eq. (5.8) provides for b = a

$$E_a^1 = \langle a^0 | \hat{V} | a^0 \rangle \tag{5.9}$$

and for $b \neq a$

$$\langle b^0 | \hat{V} | a^0 \rangle = (E_a^0 - E_b^0) \langle b^0 | a^1 \rangle \,.$$

As the states $|b^0\rangle$ form a complete system we find

$$|a^{1}\rangle = \sum_{b} |b^{0}\rangle\langle b^{0}|a^{1}\rangle = \sum_{b \text{ with } b \neq a} \frac{\langle b^{0}|V|a^{0}\rangle}{(E_{a}^{0} - E_{b}^{0})}|b^{0}\rangle$$
(5.10)

where Eq. (5.5) has been applied for b = a. Then we obtain

In first order of perturbation theory the non-degenerate state $|a^0\rangle$ exhibits

- a shift in energy by the expectation values $\langle a^0 | \hat{V} | a^0 \rangle$ of the perturbation potential for the unperturbed state.
- the admixture of other eigenstates $|b^0\rangle$ of \hat{H}_0 , see Eq. (5.2), which is dominated by states with an energy $E_b^0 \approx E_a^0$.

Multiplying Eq. (5.7) with $\langle a^0 |$ one obtains:

$$\underbrace{\langle a^0 | \hat{H}_0 | a^2 \rangle}_{=E_a^0 \langle a^0 | a^2 \rangle} + \langle a^0 | \hat{V} | a^1 \rangle = E_a^0 \langle a^0 | a^2 \rangle + E_a^1 \underbrace{\langle a^0 | a^1 \rangle}_{=0 \text{ due to Eq. (5.5)}} + E_a^2$$

and using Eq. (5.10) one obtains:

$$E_a^2 = \sum_{b \neq a} \frac{|\langle a^0 | \hat{V} | b^0 \rangle|^2}{E_a^0 - E_b^0}$$
(5.11)

Thus we find in second order perturbation theory

- The ground state is always shifted to lower energies
- Strongly coupling states (i.e. large matrix element $\langle a^0 | \hat{V} | b^0 \rangle$) which are close in energy (small $|E_b^0 - E_a^0|$) repel each other.

Example: A one-dimensional harmonic oscillator is perturbed by a quadratic term:

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 \hat{x}^2, \quad \hat{V} = \frac{1}{2}m\alpha^2 \hat{x}^2$$

Calculate the energy shift up to second order and compare the result with the exact solution.

Eqs. (5.9,5.11) provide the energy shift $E_n \approx E_n^0 + E_n^1 + E_n^2 + \dots$ with

$$\begin{split} E_n^0 &= \hbar \omega \left(n + \frac{1}{2} \right) \\ E_n^1 &= \langle n | \hat{V} | n \rangle = \frac{1}{2} m \alpha^2 \langle n | \hat{x}^2 | n \rangle \\ E_n^2 &= \sum_{k \neq n} \frac{|\langle k | \hat{V} | n \rangle|^2}{E_n^0 - E_k^0} = \left(\frac{m \alpha^2}{2} \right)^2 \sum_{k \neq n} \frac{|\langle k | \hat{x}^2 | n \rangle|^2}{E_n^0 - E_k^0} \end{split}$$

The matrix element for \hat{x}^2 have been calculated as an example in Sec. 2.1 with the result

$$\langle n+2|x^2|n\rangle = \frac{\hbar}{2m\omega}\sqrt{(n+1)(n+2)}$$
$$\langle n|x^2|n\rangle = \frac{\hbar}{2m\omega}(2n+1)$$
$$\langle n-2|x^2|n\rangle = \frac{\hbar}{2m\omega}\sqrt{n(n-1)}$$

94

5.1. STATIONARY PERTURBATION THEORY

We now get

$$\begin{split} E_n^1 = & \frac{m\alpha^2}{2} \frac{\hbar}{2m\omega} (2n+1) = \frac{1}{2} \left(\frac{\alpha}{\omega}\right)^2 \hbar\omega \left(n + \frac{1}{2}\right) \\ E_n^2 = & \left(\frac{m\alpha^2}{2} \frac{\hbar}{2m\omega}\right)^2 \left(\frac{n(n-1)}{2\hbar\omega} + \frac{(n+1)(n+2)}{-2\hbar\omega}\right) \\ = & -\frac{1}{8} \left(\frac{\alpha}{\omega}\right)^4 \hbar\omega \left(n + \frac{1}{2}\right) \end{split}$$

In our example one can calculate the eigenstates of $\hat{H}_0 + \lambda \hat{V}$ exactly as this is just a new oscillator with frequency $\sqrt{\omega^2 + \lambda \alpha^2}$. The exact eigenvalues are thus $E_n(\lambda) = \hbar \sqrt{\omega^2 + \lambda \alpha^2} (n + 1/2)$ and Taylor expansion in λ provides

$$E_n(\lambda) = \hbar\omega \left(1 + \lambda \frac{\alpha^2}{2\omega^2} - \lambda^2 \frac{\alpha^4}{8\omega^4} + \mathcal{O}\{\lambda^3\} \right) \left(n + \frac{1}{2} \right)$$

This fully agrees with $E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \mathcal{O}\{\lambda^3\}$ with coefficients E_n^j evaluated by perturbation theory.

5.1.2 Degenerate case

Now we assume that there are several states $|i, a^0\rangle$ with i = 1, 2, ..., N which are all eigenstates of \hat{H}_0 with the energy E_a^0 . This is called a degenerate level. Replacing $|a^0\rangle$ by $|i, a^0\rangle$ in Eq. (5.6) and multiplying by $\langle j, a^0 |$ provides:

$$V_{ji} \equiv \langle j, a^0 | \hat{V} | i, a^0 \rangle = E^1_{i,a} \delta_{j,i}$$
(5.12)

This is contradictory if the matrix V_{ji} is not diagonal. As V_{ji} is Hermitian, there is a set of N orthonormal columns $c_i^{(n)}$ with n = 1, 2, ..., N, which satisfy $\sum_i V_{ji} c_i^{(n)} = E_n c_j^{(n)}$. Now we choose the new eigenstates

$$|\tilde{n},a^0\rangle = \sum_i c_i^{(n)} |i,a^0\rangle$$

of \hat{H}_0 , which span the same subspace as the original states $|i, a^0\rangle$. In this basis we find

$$\langle \tilde{m}, a^0 | \hat{V} | \tilde{n}, a^0 \rangle = \sum_{i,j} c_j^{(m)*} V_{ji} c_i^{(n)} = \sum_j c_j^{(m)*} E_n c_j^{(n)} = E_n \delta_{m,n}$$

and Eq. (5.12) provides that the changes in energy in first order perturbation theory are just the eigenvalues of the matrix V_{ii} in the subspace belonging to the degenerate level E_a^0 .

This can be summarized by the following operational rules to determine the effect of the perturbation potential on an energy level E_a^0 which is degenerate.

- 1. Identify all pairwise orthonormal states $|i, a^0\rangle$ satisfying $\hat{H}_0|i, a^0\rangle = E_a^0|i, a^0\rangle$. Here i = 1, 2, ..., N, where N be the number of these states. (One calls such an energy as N-fold degenerate.) These states span the N-dimensional subspace \mathcal{M} of the ket-space.
- 2. Calculate the $N \times N$ matrix $V_{ji} = \langle j, a^0 | \hat{V} | i, a^0 \rangle$
- 3. Determine the N eigenvalues E_n and corresponding eigencolumns $c_i^{(n)}$ of the matrix V_{ji} . Apply the normalization $\sum_{j} |c_{j}^{(n)}|^{2} = 1$. 4. Construct the new states $|\tilde{n}, a^{0}\rangle = \sum_{i} c_{i}^{(n)} |i, a^{0}\rangle$ which form an alternative
- ON basis for the subspace \mathcal{M} .
- 5. The new basis states exhibit the energy shifts $E_{\tilde{n}a}^1 = E_n$ in the first order of perturbation theory.

The second order can be performed analogously to Eq. (5.11) provided that the the new basis $|\tilde{n}, a^0\rangle$ is used.

5.1.3Example: The Stark effect

Consider a hydrogen atom in an external electric field $\boldsymbol{\mathcal{E}} = \boldsymbol{\mathcal{E}} \mathbf{e}_z$. The electric potential $\phi(\mathbf{r}) = -\mathcal{E}z$ provides the perturbation

$$\hat{V} = e\mathcal{E}\hat{z}$$

taking into account the charge -e of the electron.

The **unperturbed levels** are the known states $|n, l, m\rangle$ of the hydrogen atom which are numbered by the principal quantum number n = 1, 2, ... and the angular momentum numbers l, m, where l is restricted to $l = 0, 1, \ldots n - 1$. From elementary courses we remember the energy eigenvalues

$$E_{n,l} = -\frac{\hbar^2}{2m_e a_B^2} \frac{1}{n^2} \approx -13.6eV \frac{1}{n^2}$$
(5.13)

where $a_B = 4\pi\epsilon_0 \hbar^2/(m_e e^2) \approx 0.529 \text{\AA}$ is the Bohr radius. The spatial representation of the corresponding eigenstates reads

$$\langle \mathbf{r}|n,l,m\rangle = \phi_{n,l,m}(r,\theta,\varphi) = \frac{1}{r}u_{nl}(r)Y_l^m(\theta,\varphi)$$

with the spherical harmonics $Y_l^m(\theta, \varphi)$ given on page 56. The radial functions $u_{nl}(r)$ are normalized as

$$\int_0^\infty \mathrm{d}r \, u_{n'l}(r) u_{nl}(r) = \delta_{n'n}$$

and read

$$u_{nl}(r) = \sqrt{\frac{2}{na_B}} \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}} \left(\frac{2r}{na_B}\right)^{l+1} L_{n+l}^{2l+1}\left(\frac{2r}{na_B}\right) \exp\left(-\frac{r}{na_B}\right)$$

with the Laguerre-Polynomials:

$$L_{k}^{0}(x) = e^{x} \frac{\mathrm{d}^{k}}{\mathrm{d}x^{k}} \left(x^{k} e^{-x}\right) \text{ and } L_{k}^{\mu}(x) = (-1)^{\mu} \frac{\mathrm{d}^{\mu}}{\mathrm{d}x^{\mu}} L_{k}^{0}(x)$$

In particular this provides:

$$u_{10} = \frac{2r}{\sqrt{a_B^3}} \exp\left(-\frac{r}{a_B}\right)$$
$$u_{20} = \frac{r}{\sqrt{2a_B^3}} \left(1 - \frac{r}{2a_B}\right) \exp\left(-\frac{r}{2a_B}\right) \qquad u_{21} = \frac{r}{\sqrt{6a_B^3}} \frac{r}{2a_B} \exp\left(-\frac{r}{2a_B}\right)$$

which is used in the calculations below.

The ground state n = 1 is non-degenerate. (Spin is not considered here, as it does not show any interaction with the electric field.) In the following we work in spatial representation. The first order in perturbation theory provides

$$E_{n=1}^{1} = \langle 1, 0, 0 | \hat{V} | 1, 0, 0 \rangle = \int d^{3}r \frac{1}{\sqrt{\pi a_{B}^{3}}} \exp\left(-\frac{r}{a_{B}}\right) e\mathcal{E}z \frac{1}{\sqrt{\pi a_{B}^{3}}} \exp\left(-\frac{r}{a_{B}}\right) = 0,$$

as the integrand just changes its sign for $\pm z$. The second order provides a lowering of the energy.

The **first excited state** n = 2 has a fourfold degeneracy. The corresponding states are $|1\rangle = |2, 0, 0\rangle$, $|2\rangle = |2, 1, 0\rangle$, $|3\rangle = |2, 1, -1\rangle$ and $|4\rangle = |2, 1, 1\rangle$. Now the matrix $\langle i|\hat{V}|j\rangle$ has to be determined in this subspace. Due to symmetry most of the matrix elements are zero, as shown below.

• $\langle n', l', m' | \hat{z} | n, l, m \rangle = 0$ for $m \neq m'$

Proof: As $[\hat{L}_z, \hat{z}] = [(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x), \hat{z}] = 0$ we find

$$0 = \langle n', l', m' | [\hat{L}_z, \hat{z}] | n, l, m \rangle = \hbar(m' - m) \langle n', l', m' | \hat{z} | n, l, m \rangle$$

For $m \neq m'$ one can divide by $\hbar(m'-m)$ which proofs the conjecture. \Box

• $\langle n', l, m | \hat{z} | n, l, m \rangle = 0$

Proof:

$$\langle n',l,m|\hat{z}|n,l,m\rangle = \int \mathrm{d}^3r \frac{1}{r} u_{n'l}(r) z \frac{1}{r} u_{nl}(r) \left|Y_l^m(\theta,\varphi)\right|^2$$

Under the inversion $\mathbf{r} \to -\mathbf{r}$ the absolute value r is conserved and $z \to -z$ while the spherical harmonics receive a factor $(-1)^l$. Thus the sign of the integrand changes and the total integral is zero. \Box

• Direct evaluation provides:

$$\langle 2, 0, 0|z|2, 1, 0 \rangle = \int \mathrm{d}r \, d\varphi \, \mathrm{d}\cos\theta \, r^2 \frac{1}{r} u_{20}(r) \left[Y_0^0(\theta, \varphi) \right]^* r \cos\theta \frac{1}{r} u_{21}(r) Y_1^0(\theta, \varphi)$$

$$= \int \mathrm{d}r \, \mathrm{d}\varphi \, \mathrm{d}\cos\theta \, \frac{\sqrt{3}}{4\pi} (\cos\theta)^2 \frac{r^4}{4\sqrt{3}a_B^4} \left(1 - \frac{r}{2a_B} \right) \exp\left(-\frac{r}{a_B} \right) = -3a_B$$

Together this provides the matrix

The eigenvalues are obtained from the secular equation

$$0 = \det (V_{ij} - E\delta_{i,j}) = E^2 [E^2 - 9(e\mathcal{E}a_B)^2]$$

resulting in the four eigenvalues and corresponding eigenstates

$$E_{1} = -3e\mathcal{E}a_{B} \qquad \rightarrow |\tilde{1}\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle + |2\rangle\right) \equiv \frac{1}{\sqrt{2}}\left(|2,0,0\rangle + |2,1,0\rangle\right)$$
$$E_{2} = +3e\mathcal{E}a_{B} \qquad \rightarrow |\tilde{2}\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle - |2\rangle\right) \equiv \frac{1}{\sqrt{2}}\left(|2,0,0\rangle - |2,1,0\rangle\right)$$
$$E_{3/4} = 0 \qquad \rightarrow |\tilde{3}\rangle = |3\rangle \equiv |2,1,-1\rangle, \quad |\tilde{4}\rangle = |4\rangle \equiv |2,1,1\rangle$$

98



Figure 5.1: Wavefunctions for different states of the hydrogen atom as a function for z for fixed x = 0 and y = 0. The density of the state $|\tilde{1}\rangle = (|2,0,0\rangle + |2,1,0\rangle)/\sqrt{2}$ exhibits an average shift of the electron density to the left.

Interpretation: The wave function $u_{21}(r)Y_1^0(\theta,\varphi)$ is positive for z > 0 and negative for z < 0. $u_{20}(r)Y_0^0(\theta,\varphi)$ is negative for $r > 2a_B$. Thus the superposition of both functions in the state $|\tilde{1}\rangle$ is constructive for larger negative z values and destructive for larger positive z values, see also Fig. 5.1. Thus the state $|\tilde{1}\rangle$ exhibits a shift of the electron density to negative z values, corresponding to an electric dipole moment pointing in z direction. As it is aligned with the electric field the energy of the state is lowered.

5.2 Time-dependent Perturbation Theory

In contrast to the stationary perturbation theory, where approximations for the eigenstates of the perturbed Hamiltonian are evaluated, we consider now the time dependent $|\Psi(t)\rangle$ of a system, which is prepared in the state $|\Psi(0)\rangle = |a^0\rangle$ at t = 0. Again we separate the Hamiltonian into a solvable part and a perturbation, see Eqs. (5.1,5.2). The dynamic evolution is given by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \left[\hat{H}_0 + \hat{V}(t)\right] |\Psi(t)\rangle \tag{5.14}$$

Of particular interest is the probability $P_b(t)$ to find the system in another eigenstate $|b^0\rangle$ of \hat{H}_0 at a later time t, which can be evaluated via

$$P_b(t) = |\langle b^0 | \Psi(t) \rangle|^2 \quad \text{for} \quad |\Psi(0)\rangle = |a^0\rangle$$
(5.15)

Without the perturbation (i.e. $\hat{V} = 0$), we find $|\Psi(t)\rangle = e^{-iE_a^0 t/\hbar} |a^0\rangle$, as $|a^0\rangle$ is an eigenstate of \hat{H}_0 . Thus $P_b(t) = 0$ for $b \neq a$ while $P_a(t) = 1$ and the system stays

in state $|a^0\rangle$ forever. However, for a finite perturbation $\hat{V}(t)$, the state $|a^0\rangle$ is no longer an eigenstate of the full Hamiltonian (5.1) and the time-dependent solution of the Schrödinger equation provides admixtures by different states $|b^0\rangle$.

In order to evaluate $|\Psi(t)\rangle$ perturbatively, it is convenient to apply the interaction picture. This concept is of rather general use in quantum mechanics and will be introduced in section 5.2.1. It significantly simplifies the calculation so that the general result can be directly obtained in section 5.2.2.

5.2.1 Interaction picture (Dirac picture)

For $\hat{H} = \hat{H}_0$ the time-dependence of an arbitrary state $|\Psi(t)\rangle$ is given by, see Eq.(1.38):

$$\begin{split} |\Psi(t)\rangle &= \sum_{a} c_{a} \exp\left(-\mathrm{i}\frac{E_{a}^{0}t}{\hbar}\right) |a^{0}\rangle = \sum_{b} |b^{0}\rangle \exp\left(-\mathrm{i}\frac{E_{b}^{0}t}{\hbar}\right) \langle b^{0}| \sum_{a} c_{a}|a^{0}\rangle \\ &= \exp\left(-\mathrm{i}\frac{\hat{H}_{0}t}{\hbar}\right) |\Psi(t=0)\rangle \end{split}$$

where the definition (1.29) for a function of an operator was used. In order to treat the perturbation $\hat{V}(t)$ we want to treat the dynamics of \hat{H}_0 exactly. Thus we make the ansatz:

$$|\Psi(t)\rangle = \exp\left(-i\frac{\hat{H}_{0}t}{\hbar}\right)|\Psi^{D}(t)\rangle$$

where $|\Psi^D(t)\rangle$ is the ket in the *interaction picture* (also Dirac-picture, thus we use the index D). With Eq. (5.14) we obtain

$$\begin{split} \mathrm{i}\hbar\frac{\partial}{\partial t}|\Psi^{D}(t)\rangle &=\mathrm{i}\hbar\frac{\partial}{\partial t}\left[\exp\left(\mathrm{i}\frac{\hat{H}_{0}t}{\hbar}\right)|\Psi(t)\rangle\right]\\ &=-\hat{H}_{0}\exp\left(\mathrm{i}\frac{\hat{H}_{0}t}{\hbar}\right)|\Psi(t)\rangle + \exp\left(\mathrm{i}\frac{\hat{H}_{0}t}{\hbar}\right)\left(\hat{H}_{0}+\hat{V}(t)\right)|\Psi(t)\rangle\\ &=\hat{V}^{D}(t)|\Psi^{D}(t)\rangle \end{split}$$
(5.16)

where we used the fact that $[\hat{H}_0, \exp(i\hat{H}_0 t/\hbar)] = 0$, and defined the operator in interaction-picture

$$\hat{V}^{D}(t) = \exp\left(i\frac{\hat{H}_{0}t}{\hbar}\right)\hat{V}(t)\exp\left(-i\frac{\hat{H}_{0}t}{\hbar}\right)$$
(5.17)

In the interaction picture all states and operators have a modified time dependence. Thereby \hat{H}_0 does not appear in the equation of motion (5.16) for the states.

5.2.2 Result

Using the initial state $|\Psi(0)\rangle = |a^0\rangle$ at t = 0, the differential equation (5.16) can be formally integrated as

$$|\Psi^D(t)\rangle = |a^0\rangle + \frac{1}{\mathrm{i}\hbar} \int_0^t \mathrm{d}t' \,\hat{V}^D(t') |\Psi^D(t')\rangle \tag{5.18}$$

We find that for short times and small perturbations $V = \langle \hat{V}^D(t') \rangle$, the state hardly changes and thus one may expand

$$|\Psi^D(t)\rangle = |a^0\rangle + \mathcal{O}\left\{\frac{Vt}{\hbar}\right\}$$

Inserting this into the integrand in Eq. (5.18) providing

$$|\Psi^{D}(t)\rangle = |a^{0}\rangle + \frac{1}{\mathrm{i}\hbar} \int_{0}^{t} \mathrm{d}t' \,\hat{V}^{D}(t') |a^{0}\rangle + \mathcal{O}\left\{\left(\frac{Vt}{\hbar}\right)^{2}\right\}$$
(5.19)

We are now interested in the probability $P_b(t)$ to find the system in state $|b^0\rangle$ at time t, which is given by $|\langle b^0 | \Psi(t) \rangle|^2$

$$P_b(t) = |\langle b^0 | \Psi(t) \rangle|^2 = |\langle b^0 | e^{-iE_b t/\hbar} | \Psi(t) \rangle|^2 = |\langle b^0 | e^{-i\hat{H}_0 t/\hbar} | \Psi(t) \rangle|^2 = |\langle b^0 | \Psi_D(t) \rangle|^2$$

where we used $\langle b^0 | \hat{H}_0 = \langle b^0 | E_b^0$. Thus we find for $b \neq a$ in lowest order in \hat{V} .

$$P_b(t) = \left| \frac{1}{\mathrm{i}\hbar} \int_0^t \mathrm{d}t' \left\langle b^0 | \hat{V}^D(t') | a^0 \right\rangle \right|^2 \tag{5.20}$$

This result is commonly used if one wants to study the impact of short laser pulses on atomic states. If the pulse has a finite duration T, it follows $\hat{V}^D(t') = 0$ for t' > T and $P_b(t)$ is constant for t > T. Thus the transition probabilities only change while the perturbation signal is active.

5.2.3 Action of a laser pulse on a hydrogen atom

A hydrogen atom is in the ground state $|g\rangle = |n = 1, l = 0, m = 0\rangle$ for t = 0. A short laser pulse of duration τ with the electric field $\boldsymbol{\mathcal{E}}(t) = \mathcal{E}_0 \sin(\omega t) \mathbf{e}_z$ provides the perturbation potential

$$\hat{V}(t) = e\mathcal{E}_0 \sin(\omega t)\hat{z}$$

for the time interval $0 < t < \tau$. Here we want to calculate the *probability* P to find the atom in the state $|e\rangle = |n = 2, l = 1, m = 0\rangle$ after the pulse.

In order to apply Eq. (5.20), we have to evaluate $\langle e|\hat{V}^D(t')|g\rangle$. Inserting Eq. (5.17) and using

$$\exp\left(-\mathrm{i}\frac{\hat{H}_{0}t'}{\hbar}\right)|g\rangle = \exp\left(-\mathrm{i}\frac{E_{1}t'}{\hbar}\right)|g\rangle \quad \text{and} \quad \langle e|\exp\left(\mathrm{i}\frac{\hat{H}_{0}t'}{\hbar}\right) = \exp\left(\mathrm{i}\frac{E_{2}t'}{\hbar}\right)\langle e|g\rangle$$

which follow immediately from Eq. (1.29) if one applies the eigenstates $|n, l, m\rangle$ of \hat{H}_0 , we find

$$\langle e|\hat{V}^{D}(t')|g\rangle = \frac{\mathrm{e}^{\mathrm{i}(\omega_{eg}+\omega)t'} - \mathrm{e}^{\mathrm{i}(\omega_{eg}-\omega)t'}}{2\mathrm{i}} e\mathcal{E}_{0}\langle e|\hat{z}|g\rangle \quad \text{with} \quad \omega_{eg} = \frac{E_{e} - E_{g}}{\hbar} = 1.55 \times 10^{16}/\mathrm{s}$$

Using the expression from pages 56 and 97, the matrix element reads

$$\begin{aligned} \langle e|\hat{z}|g\rangle &= \int r^{2}\sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi \,\frac{u_{21}(r)}{r}Y_{1}^{0}(\theta,\varphi)r\cos\theta\frac{u_{10}(r)}{r}Y_{0}^{0}(\theta,\varphi) \\ &= \int_{0}^{\infty}\mathrm{d}r \int_{-1}^{1}\mathrm{d}\cos\theta \int_{0}^{2\pi}\mathrm{d}\varphi \frac{r^{4}}{4\sqrt{2\pi}a_{B}^{4}}\cos^{2}\theta\mathrm{e}^{-3r/2a_{B}} = \int_{0}^{\infty}\mathrm{d}r\frac{r^{4}}{3\sqrt{2}a_{B}^{4}}\mathrm{e}^{-3r/2a_{B}} \\ &= \frac{2^{7}\sqrt{2}}{3^{5}}a_{B} \end{aligned}$$

Together this provides us with the transition probability

$$P = \left(\frac{2^{7}\sqrt{2}e\mathcal{E}_{0}a_{B}}{3^{5}\hbar}\right)^{2} \left|\int_{0}^{\tau} dt' \frac{e^{i(\omega_{eg}+\omega)t'} - e^{i(\omega_{eg}-\omega)t'}}{2i}\right|^{2}$$
(5.21)
$$= \left(\frac{2^{7}\sqrt{2}e\mathcal{E}_{0}a_{B}}{3^{5}\hbar}\right)^{2} \left|-\frac{e^{i(\omega_{eg}+\omega)\tau} - 1}{2(\omega_{eg}+\omega)} + \frac{e^{i(\omega_{eg}-\omega)\tau} - 1}{2(\omega_{eg}-\omega)}\right|^{2}$$
$$= \left(\frac{2^{7}\sqrt{2}e\mathcal{E}_{0}a_{B}}{3^{5}\hbar}\right)^{2} \left|-ie^{i(\omega_{eg}+\omega)\tau/2}\frac{\sin((\omega_{eg}+\omega)\tau/2)}{\omega_{eg}+\omega} + ie^{i(\omega_{eg}-\omega)\tau/2}\frac{\sin((\omega_{eg}-\omega)\tau/2)}{\omega_{eg}-\omega}\right|^{2}$$
(5.22)

102


Figure 5.2: Transition probability according to Eq. (5.22) for a laser pulse with $\mathcal{E}_0 = 10^{10}$ V/m and a duration of 5 cycles, i.e. $\tau = 10\pi/\omega$. (Such 'attosecond' pulses with few cycles are a topic of research at the division of atomic physics in Lund.)

In Figure 5.2 the probability is plotted for a pulse with 5 cycles. We find that the transition probability peaks around the resonance frequency $\omega \approx \omega_{eg}$. For other frequencies, the oscillatory terms $e^{i(\omega_{eg}+\omega)t'}$ and $e^{i(\omega_{eg}-\omega)t'}$ in Eq. (5.21) provide no result for sufficiently long integration times τ . Indeed the width of the peak around $\omega \approx \omega_{eg}$ is of the order $1/\tau$.

As $P \propto \mathcal{E}_0^2$, see Eq. (5.22), the probability become four times larger, if one doubles the laser field strength. In the case of Fig. 5.2, this provides probabilities above one, which are clearly wrong. This indicates the breakdown of the perturbation theory, as the higher order terms in Eq. (5.19) become of crucial relevance.

5.3 Fermi's Golden Rule

The t'-integral in Eq. (5.20) is easily solvable for fictitious perturbations of the form

$$\hat{V}(t) = \hat{F} e^{-i\omega t}$$

resulting in the transition-probability

$$P_b(t) = |\langle b^0 | \hat{F} | a^0 \rangle|^2 D_t \left(E_b^0 - E_a^0 - \hbar \omega \right) \quad \text{for} \quad b \neq a \tag{5.23}$$

with the auxiliary function

$$D_{t}(\Delta E) = \left| \frac{1}{\hbar} \int_{0}^{t} dt' e^{i\Delta Et'/\hbar} \right|^{2} = \left| \frac{e^{i\Delta Et/\hbar} - 1}{i\Delta E} \right|^{2}$$
$$= \left| e^{i\frac{\Delta E}{2}t/\hbar} \frac{e^{i\frac{\Delta E}{2}t/\hbar} - e^{-i\frac{\Delta E}{2}t/\hbar}}{i\Delta E} \right|^{2} = \frac{4\sin^{2}\left(\frac{\Delta E}{2}t/\hbar\right)}{\Delta E^{2}}$$
(5.24)

Figure 5.3: The function $D_t(\Delta E)$ from $\sum_{n=1}^{\infty} 0.6$ Eq. (5.24). As $\hbar = 0.66 eV/fs$ the energy scale is 0.66 meV for t = 1 ps (semiconductors), 0.66 eV for t = 1 fs (molecules), 0.2 and 0.66 MeV for $t = 10^{-21}$ s (high energy physics).



Figure 5.3 shows that $D_t(\Delta E)$ has large values only for $-2\pi\hbar/t < \Delta E < 2\pi\hbar/t$, where the maximum $D_t(0) = t^2/\hbar^2$ increases rapidly with time. Furthermore a glance to a table of integrals gives $\int_{-\infty}^{\infty} dx D_t(x) = 2\pi t/\hbar$. Thus we define the function

$$\delta_t(\Delta E) = \frac{\hbar}{2\pi t} D_t \left(\Delta E\right)$$

which is a representation of the δ -function in the limit $t \to \infty$. Now we consider two typical cases:

(i) Setting $\omega = 0$, i.e. considering a constant potential $\hat{V}(t) = \hat{V}$, we obtain from Eq. (5.23)

$$P_{a\to b}(t) = \frac{2\pi t}{\hbar} |\langle b^0 | \hat{V} | a^0 \rangle|^2 \delta_t (E_b^0 - E_a^0)$$
(5.25)

(ii) Now we consider periodic perturbation potentials. Being a part of the Hamiltonian, $\hat{V}(t)$ is a Hermitian operator, The most general form of a Hermitian operator containing a single frequency component ω is

$$\hat{V}(t) = \hat{F} e^{-i\omega t} + \hat{F}^{\dagger} e^{i\omega t}$$

Treating both terms separately (which is possible for $t \gg \omega/2\pi$, where the δ_t functions do not overlap) we obtain

$$P_{a\to b}(t) = \frac{2\pi t}{\hbar} |\langle b^0 | \hat{F} | a^0 \rangle|^2 \delta_t (E_b^0 - E_a^0 - \hbar\omega) + \frac{2\pi t}{\hbar} |\langle b^0 | \hat{F}^\dagger | a^0 \rangle|^2 \delta_t (E_b^0 - E_a^0 + \hbar\omega) \,.$$
(5.26)

The function $\delta_t(\Delta E)$ can be replaced by a δ -function, if the following conditions are met:

- There is an integration over a continuum of final states $|b^0\rangle$ or frequencies ω with amplitude F_{ω} , as the δ -function is only properly defined together with an integral over its argument.
- The observation time t is sufficiently long, so that the matrix element $|\langle b^0 | \hat{V} | a^0 \rangle|^2$ (or $|\langle b^0 | \hat{F}_{\omega} | a^0 \rangle|^2$) is approximately constant within the energy range $|E_b^0 - E_a^0 \pm \hbar \omega| \lesssim 2\pi \hbar/t$ of the allowed final states b (or frequencies ω).
- The perturbation \hat{V} is sufficiently weak, so that the probability to reach any possible state $\sum_{b\neq a} P_b(t)$ does not reach unity within the observation time.

Replacing $\delta_t(\Delta E)$ by $\delta(E)$ in Eqs. (5.25,5.26) we find that $P_b(t)$ increases linearly in time and it makes sense to define $\Gamma_{a\to b} = P_b(t)/t$ as the transition rate from state *a* to state *b*. This provides

Fermi's golden rule: For a time-independent perturbation potential \hat{V} the transition rate from state a

For a time-independent perturbation potential V the transition rate from state to state b is given by

$$\Gamma_{a\to b} = \frac{2\pi}{\hbar} |\langle b^0 | \hat{V} | a^0 \rangle|^2 \delta(E_b^0 - E_a^0)$$
(5.27)

Thus transitions require the same energy of the initial and final state. A *periodic perturbation potential* $\hat{V}(t) = \hat{F} e^{-i\omega t} + \hat{F}^{\dagger} e^{i\omega t}$ with frequency ω provides

$$\Gamma_{a\to b} = \frac{2\pi}{\hbar} |\langle b^0 | \hat{F} | a^0 \rangle|^2 \delta(E_b^0 - E_a^0 - \hbar\omega) + \frac{2\pi}{\hbar} |\langle b^0 | \hat{F}^\dagger | a^0 \rangle|^2 \delta(E_b^0 - E_a^0 + \hbar\omega) .$$
(5.28)

In this case transitions are only possible if the energy of the final state is $\hbar\omega$ higher/lower than the energy of the initial state. This corresponds to the *absorption/emission* of the *energy quantum* $\hbar\omega$ from/to the oscillating field, respectively.

Note that Fermi's golden rule provides a constant transition rate, i.e., a linear increase of the probability $P_b(t)$ for the system to be found in the new state. This essentially differs from the behavior found for the Rabi oscillation (see exercise), where $P_b(t) \propto \sin^2(\Omega_R t/2)$, and thus in the beginning $P_b(t) \propto t^2$ is found. The reason for this difference is that one has a system with two states and a fixed frequency in the Rabi oscillation scenario. Thus there is neither a continuum of final states $|b^0\rangle$ nor of frequencies ω , as required for the replacement of $\delta_t(E_b^0 - E_a^0 + \hbar\omega)$ in Eq. (5.26) by $\delta(E_b^0 - E_a^0 + \hbar\omega)$. Indeed, from the definition (5.24) of

 $D_t(E_b^0 - E_a^0 + \hbar\omega)$, we recover the correct initial power law $P_b(t) \propto t^2$, if the laser field is in resonance with the energy difference of both states.

5.3.1 Example: β -decay of the neutron

Nuclei are eigenstates of the strong interaction but not necessarily eigenstates of the weak interaction, which causes transitions between different nuclei. For the β -decay of the neutron the following many-particle states are of relevance:

- A neutron (in rest): State $|a^0\rangle$ with energy $E_a^0 = m_n c^2$
- A proton (almost in rest) + free electron with wave vector k_e + free antineutrino with wave vector k_ν:

State $|b^0\rangle = |\mathbf{k}_e, \mathbf{k}_\nu\rangle$ with energy

$$E_b^0 = m_p c^2 + \sqrt{m_e^2 c^4 + \hbar^2 c^2 k_e^2} + \sqrt{m_\nu^2 c^4 + \hbar^2 c^2 k_\nu^2}$$

where we take into account a possible finite mass m_{ν} of the neutrinos.²

In addition we assume that the matrix element $|\langle \mathbf{k}_e, \mathbf{k}_\nu | \hat{V}_{\text{weak interaction}} | a^0 \rangle|^2 = g^2$ is constant. (This is a point-interaction, as assumed by Enrico Fermi 1934.) In a typically experiment, the momentum $\mathbf{p}_e = \hbar \mathbf{k}_e$ of the final electron is measured. Thus, we want to evaluate the transition rate to a final state \mathbf{k}_e with arbitrary \mathbf{k}_ν

$$\Gamma_{a \to \mathbf{k}_{e}} = \int \underbrace{\mathrm{d}^{3}k_{\nu}}_{4\pi k_{\nu}^{2}\mathrm{d}k_{\nu}} \frac{2\pi}{\hbar} g^{2} \delta \left(\underbrace{(m_{p} - m_{n})c^{2} + \sqrt{m_{e}^{2}c^{4} + \mathbf{p}_{e}^{2}c^{2}}}_{=-A(\mathbf{p}_{e})} + \sqrt{m_{\nu}^{2}c^{4} + \hbar^{2}c^{2}k_{\nu}^{2}} \right)$$

Now, we use the relation

$$\int_{a}^{b} \mathrm{d}x \, g(x) \delta(f(x)) = \sum_{i} \frac{g(x_i)}{|f'(x_i)|} \text{ where } f(x_i) = 0 \text{ with } a < x_i < b$$

and define the step function by $\Theta(x) = 1$ for x > 0 and $\Theta(x) = 0$ for x < 0. After a few lines of algebra we find:

$$\Gamma_{a \to \mathbf{k}_e} = \frac{8\pi^2 g^2}{\hbar^4 c^3} A(\mathbf{p}_e) \sqrt{A(\mathbf{p}_e)^2 - m_\nu^2 c^4} \,\Theta(A(\mathbf{p}_e) - m_\nu c^2)$$

²As indicated by Neutrino oscillations. Nobel price 2002 to R. Davis, M. Koshiba, and R. Giacconi, http://nobelprize.org/nobel_prizes/physics/laureates/2002/phyadv02.pdf)



Figure 5.4: Probability (in arbitrary units) to find a specific momentum \mathbf{p}_e of the electron after the neutron decay assuming different masses of the antineutrino.

which shows a characteristic momentum dependence for small A (i.e. close to the maximum electron momentum), as displayed in Fig. 5.4. Fitting to experimental data provides a rather small upper limit for the neutrino mass, currently $2\text{eV}/c^2$ from the β -decay of Tritium³. (Note that for such small energies the kinetic energy of the final nucleus becomes relevant, which was neglected for simplicity here.)

5.3.2 Example: Radiation transitions

Consider a hydrogen atom with the Hamilton operator

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}|}$$

where the eigenstates are given by $|a^0\rangle = |n, l, m, m_s\rangle$ with principal quantum number n, and the quantum numbers for total angular momentum l, its projection to the z axis m_l , as well as spin projection m_s . An electromagnetic wave (light) with frequency ω can be described by the electromagnetic potentials (in Coulomb gauge $\nabla \cdot \mathbf{A} = 0$)

$$\mathbf{A}(\mathbf{r},t) = \frac{1}{\omega} \mathbf{E}_0(\omega) \cos(\mathbf{k}(\omega) \cdot \mathbf{r} - \omega t) \quad \text{and} \quad \varphi(\mathbf{r},t) = 0$$

 $^{^3\}mathrm{according}$ to the Particle Data Group, W-M Yao et al., J. Phys. G: Nucl. Part. Phys. **33** 1 (2006)

Eqs. (3.11,4.4) provide the Hamilton-Operator (here e > 0 is the elementary charge).

$$\begin{aligned} \hat{H} &= \frac{[\hat{\mathbf{p}} + e\mathbf{A}(\mathbf{r}, t)]^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}|} + g_e \frac{e}{2m_e} \hat{\mathbf{S}} \cdot \mathbf{B}(\mathbf{r}, t) \\ &= \hat{H}_0 + \frac{e}{m_e \omega} \mathbf{E}_0(\omega) \cdot \hat{\mathbf{p}} \frac{1}{2} \left(e^{i(\mathbf{k}(\omega) \cdot \mathbf{r} - \omega t)} + e^{-i(\mathbf{k}(\omega) \cdot \mathbf{r} - \omega t)} \right) \\ &+ g_e \frac{e}{2m_e} \hat{\mathbf{S}} \cdot \left[\mathbf{k}(\omega) \times \mathbf{E}_0(\omega) \frac{i}{2\omega} \left(e^{i(\mathbf{k}(\omega) \cdot \mathbf{r} - \omega t)} - e^{-i(\mathbf{k}(\omega) \cdot \mathbf{r} - \omega t)} \right) \right] + \mathcal{O}(E_0^2) \end{aligned}$$

For visible light we have $k = 2\pi/\lambda \sim 2\pi/600$ nm. In contrast the atomic size is of the order $\sim a_B = 0.0529$ nm, and atomic momenta are of the order \hbar/a_B . Thus terms with kr (in the exponent) as well as the spin-term ($Sk \sim \hbar 2\pi/600$ nm $\ll p$) are negligible in a first approximation.

The transition rate between two atomic levels a and b is given by Eq. (5.26)

$$\Gamma_{a\to b}(t) = \frac{2\pi}{\hbar} \left| \frac{e}{2m_e \omega} \langle b^0 | \mathbf{E}_0(\omega) \cdot \hat{\mathbf{p}} | a^0 \rangle \right|^2 \left[\delta_t (E_b^0 - E_a^0 - \hbar \omega) + \delta_t (E_b^0 - E_a^0 + \hbar \omega) \right]$$

Thus, the radiation field is exchanging energy in portions of $\hbar\omega$ (*photons*) with the atom. Accordingly the processes are called absorption and emission of a photon by the atoms.

The size of the transition rate is given by the matrix element, which for $|a^0\rangle = |n, l, m, m_s\rangle$ and $|b^0\rangle = |n', l', m', m'_s\rangle$ is given by

$$\langle b^{0} | \hat{\mathbf{p}} | a^{0} \rangle = \langle n', l', m', m'_{s} | m_{e} \frac{\mathbf{i}}{\hbar} [\hat{H}_{0}, \hat{\mathbf{r}}] | n, l, m, m_{s} \rangle$$
$$= m_{e} \frac{\mathbf{i}}{\hbar} (E_{n'l'}^{0} - E_{nl}^{0}) \underbrace{\langle n', l', m', m'_{s} | \hat{\mathbf{r}} | n, l, m, m_{s} \rangle}_{= -\frac{1}{e} \mathbf{d}_{ba}}$$

Using the properties of the spherical harmonics, one finds that the *dipole matrix* element $\mathbf{d}_{ba} = 0$ vanishes unless $l' = l \pm 1$, $m'_s = m_s$ and $m' = \in \{m - 1, m, m + 1\}$.

5.3. FERMI'S GOLDEN RULE

For an atom interacting with electromagnetic radiation of frequency ω the transition rate reads

$$\Gamma_{a\to b} = \frac{2\pi}{\hbar} \left| \frac{\mathbf{E}_0 \cdot \mathbf{d}_{ba}}{2} \right|^2 \left[\delta_t (E_b^0 - E_a^0 - \hbar\omega) + \delta_t (E_b^0 - E_a^0 + \hbar\omega) \right] \,.$$

between the atomic levels a and b in dipole approximation $(e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1 \text{ and } \hbar k \ll p)$. The possible processes are the **induced absorption** and the **induced emission** of a photon. Both processes exhibit the same rate. The *selection rules* are $\Delta l = \pm 1$, $\Delta m = 0, \pm 1$ and $\Delta m_s = 0$.

Remarks:

- Taking into account the **quantization** of the electromagnetic field we have $\hat{F}^{\dagger} \neq \hat{F}$ and the transition rates differ for emission and absorption. This can be described by the additional **spontaneous emission**, which is also possible if the electromagnetic field is in its ground state (the vacuum fluctuations of the field constitute the perturbation potential).
- Looking at the dipole matrix elements, we find

$$\mathbf{e}_{z} \cdot \mathbf{d}_{ba} = \begin{cases} \neq 0 & \text{for } \Delta m = 0 \\ = 0 & \text{for } \Delta m = \pm 1 \end{cases} \quad \mathbf{e}_{x/y} \cdot \mathbf{d}_{ba} = \begin{cases} = 0 & \text{for } \Delta m = 0 \\ \neq 0 & \text{for } \Delta m = \pm 1 \end{cases}$$

Within the basis $|l, m\rangle$ of the angular momentum eigenstates the z-axis stands out, as \hat{L}_z is diagonal. For light propagating in the z-direction, the z-component of \mathbf{E}_0 vanishes and we only find transitions with $\Delta m = \pm 1$. This is consistent with the intrinsic angular momentum $\pm \hbar$ of photons in the direction of propagation,⁴ which is transferred in the absorption or emission process.

 If one takes into account higher order terms e^{ik·r} ≈ 1 + ik · r, one obtains the electrical quadrupole and magnetic dipole transitions. The latter also include the spin-term in Eq. (5.3.2). In both cases one obtains different selection rules than for dipole approximation but the rates are several orders of magnitude smaller because of the reduced matrix elements.

⁴see, e.g. Section 4B of G. Grynberg, A. Aspect, and C. Fabre *Introduction to Quantum Optics* (Cambridge University Press, 2010).

5.4 Decay within a simple model^{*}

Here we want to shed light into the meaning of the transition rate in Fermi's golden rule. Within a simple model, we show the following:

- Fermi's golden rule leads to an exponential decay of the probability that the initial state is occupied with the rate Γ. Here Γ is the sum of transition rates to all possible states.
- The final states are distributed over a certain energy range with a Lorentzian distribution function with a full width at half maximum $\hbar\Gamma$.
- Fermi's golden rule is valid if the finite states form a continuum or, in the case of discrete states, are densely spaced with a separation in energy significantly lesser than ħΓ. In addition the finite states must cover an energy range which is significantly larger than ħΓ.

For this purpose we consider the following model: An initial state $|i\rangle$ with energy E_i is coupled to states $|k\rangle$ with energy $E_i + k\hbar\epsilon$ and matrix elements $\langle k|\hat{V}|i\rangle = w$, where $k = -N, -N+1, \ldots N$. Using Fermi's golden rule (5.27), the total transition rate Γ to any of the final states k is given by

$$\Gamma = \sum_{k} \Gamma_{i \to k} = \frac{2\pi}{\hbar} \sum_{k} |w|^2 \delta(E_k - E_i) = \frac{2\pi |w|^2}{\hbar^2 \epsilon} \int dE_k \delta(E_k - E_i) = \frac{2\pi |w|^2}{\hbar^2 \epsilon}$$
(5.29)

where we used $\hbar \epsilon \sum_k \to \int dE_k$ which is justified for small energy spacings $\hbar \epsilon$. Now we perform an exact treatment beyond perturbation theory for comparison. The interaction picture Eq. (5.16) provides the equations of motion for the expansion coefficients $f_k(t) = \langle k | \Psi^D(t) \rangle$ and $f_i(t) = \langle i | \Psi^D(t) \rangle$:

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} f_k(t) = w \mathrm{e}^{\mathrm{i}k\epsilon t} f_i(t) \quad i\hbar \frac{\mathrm{d}}{\mathrm{d}t} f_i(t) = \sum_k w^* \mathrm{e}^{-\mathrm{i}k\epsilon t} f_k(t)$$

For the initial condition $f_k(0) = 0$, we find

$$f_k(t) = \frac{w}{\mathrm{i}\hbar} \int_0^t \mathrm{d}t' \mathrm{e}^{\mathrm{i}k\epsilon t'} f_i(t')$$

and thus

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} f_i(t) = \frac{|w|^2}{i\hbar} \int_0^t \mathrm{d}t' \sum_k \mathrm{e}^{-\mathrm{i}k\epsilon(t-t')} f_i(t') = \frac{|w|^2}{i\hbar} \int_0^t \mathrm{d}\tau \sum_k \mathrm{e}^{-\mathrm{i}k\epsilon\tau} f_i(t-\tau) \quad (5.30)$$

Now we have

$$\sum_{k=-N}^{N} e^{-ik\epsilon\tau} = e^{-iN\epsilon\tau} \sum_{k'=0}^{2N} e^{-ik'\epsilon\tau} = e^{-iN\epsilon\tau} \frac{e^{-i(2N+1)\epsilon\tau} - 1}{e^{-i\epsilon\tau} - 1} = \frac{\sin((2N+1)\epsilon\tau/2)}{\sin(\epsilon\tau/2)}$$
$$\approx \frac{2}{\epsilon\tau} \sin\left(\frac{(2N+1)\epsilon\tau}{2}\right) \equiv g(\tau)$$

where we assumed $\tau \ll 1/\epsilon$ (condition I). Now this auxiliary function $g(\tau)$ satisfies $\int_0^\infty d\tau g(\tau) = \pi/\epsilon$, where the main contribution is from the range $0 \le \tau < \frac{2\pi}{(2N+1)}\epsilon$. Indeed, one can show that

$$\frac{\epsilon}{\pi} \left| \int_0^T g(\tau) - \frac{\pi}{\epsilon} \right| < \frac{2}{(2N+1)\epsilon T} \quad \text{(not the best bound)}$$

If now the function $f_i(t-\tau)$ is approximately constant on the time scale $\tau \lesssim \frac{2\pi}{(2N+1)\epsilon}$ (*condition II*), we may replace $f_i(t-\tau)$ by $f_i(t)$ in Eq. (5.30). Then this differential equation is easily solved and provides for the initial condition $f_i(0) = 1$:

$$f_i(t) = e^{-\Gamma t/2}$$
 with $\Gamma = \frac{2\pi |w|^2}{\hbar^2 \epsilon}$ (5.31)

Thus the occupation probability of the initial state $|f_i(t)|^2$ decays with the rate Γ , which is the sum of rates from Fermi's golden rule.

Finally, we find

$$f_k(t) = \frac{w}{i\hbar} \int_0^t dt' e^{ik\epsilon t'} e^{-\Gamma t'/2} = \frac{w}{i\hbar} \frac{1}{ik\epsilon - \Gamma/2} \left(e^{ik\epsilon t - \Gamma t/2} - 1 \right)$$

which provides the occupation probability

$$|f_k(t)|^2 = \frac{\epsilon}{2\pi} \frac{\Gamma}{(k\epsilon)^2 + \Gamma^2/4} = \frac{\epsilon\hbar}{2\pi} \frac{\hbar\Gamma}{(E_k - E_i)^2 + \hbar^2\Gamma^2/4} \quad \text{for} \quad t \gg \frac{1}{\Gamma}.$$
 (5.32)

Thus the initial state is spread towards different final states with energies in the range $|E_k - E_i| \leq \hbar\Gamma$. The distribution function in energy is a Lorentzian with a full width at half maximum (FWHM) of $\hbar\Gamma$.

Eqs. (5.31,5.32) show, that the initial state decays on the time $1/\Gamma$, which allows us to quantify the two conditions for the approximations used above.

- **Condition I** For consistency, the time difference $\tau = t t'$ must cover the range of several decay times $1/\Gamma$. Thus we need $\epsilon \ll 1/\Gamma$. Physically, this means that the spacing between the final levels must be significantly smaller than $\hbar\Gamma$. Furthermore, the total observation time must not surpass $1/\epsilon$. (Alternatively, we can assume a dephasing of the final levels within this time scale due to processes not included here)
- **Condition II** As $f_i(t)$ is changing on the time-scale $1/\Gamma$, we require $1/\Gamma \gg \frac{2\pi}{(2N+1)\epsilon}$ or $N\epsilon\hbar \gg \hbar\Gamma$. Thus the final states must cover a range of several $\hbar\Gamma$ around the energy of the initial state. This makes sense, as such a range is also finally occupied, see Eq. (5.32).

Chapter 6

MANY-PARTICLE QUANTUM MECHANICS

Real systems are always based on interacting particles. Up till now we studied single particles in the presence of external potentials which are in fact an approximation for the interaction with the rest of the world, see, e.g. Sec. 2.4.1. Now we focus on systems of interacting particles, which constitute already a big problem in classical physics. A particular problem arises in quantum mechanics if we consider *identical* particles exhibiting the same physical properties (such as mass, charge, etc) so that one cannot distinguish them in any type of measurement. Thus we have to consider two cases seperately: (i) distinguishable particles like the proton and the electron in a hydrogen atom, (ii) identical particles like several electrons in an external confinement.

6.1 Distinguishable Particles

In analogy to the case of positronium (Sec. 3.4.2) we define the quantum state $|\Psi\rangle$ of a system of N distinguishable particles (numbered by 1, 2, ..., N) as an element of the *product space* $\mathcal{H}_1 \otimes \mathcal{H}_2 \otimes ... \otimes \mathcal{H}_N$ which is spanned by the basis $\{|\varphi_{n_1}^{(1)}\rangle \otimes |\varphi_{n_2}^{(2)}\rangle \otimes ..., |\varphi_{n_N}^{(N)}\rangle\}$. Here $\{|\varphi_n^{(i)}\rangle\}$ is a ON basis of the ket space \mathcal{H}_i for the particle of sort *i*. Thus, any N-particle state $|\Psi\rangle$ is uniquely defined by the

complex expansion coefficients c_{n_1,n_2,\ldots,n_N} via

$$|\Psi\rangle = \sum_{n_1,\dots,n_N} c_{n_1,n_2,\dots,n_N} |\varphi_{n_1}^{(1)}\rangle \otimes |\varphi_{n_2}^{(2)}\rangle \otimes \dots \otimes |\varphi_{n_N}^{(N)}\rangle$$
(6.1)

In the following, we restrict to two-particle states for convenience. The generalization to larger numbers N is straightforward.

The bases states $|\varphi_n^{(1)}\rangle \otimes |\varphi_m^{(2)}\rangle$ are supposed to form an ON basis of the product space, so that their inner product is defined as

$$(\langle \varphi_{n'}^{(1)} | \otimes \langle \varphi_{m'}^{(2)} |) (|\varphi_n^{(1)}\rangle \otimes |\varphi_m^{(2)}\rangle) = \langle \varphi_{n'}^{(1)} | \varphi_n^{(1)}\rangle \langle \varphi_{m'}^{(2)} | \varphi_m^{(2)}\rangle = \delta_{n'n} \delta_{m'm}$$
(6.2)

Exploiting the linearity of the inner product, this defines the inner product of arbitrary many-particle states from the same product space.

6.1.1 Product states versus entanglement

Note, that only few elements of the product space are *product states*, i.e. they can be written as a single direct product

$$|\Psi\rangle_{\text{Product state}} = |\psi^{(1)}\rangle \otimes |\phi^{(2)}\rangle$$

with appropriate states $|\psi^{(1)}\rangle, |\phi^{(2)}\rangle$ from the respective single particle spaces. Expanding $|\psi^{(1)}\rangle = \sum_n a_n |\varphi_n^{(1)}\rangle$ and $|\phi^{(2)}\rangle = \sum_m b_m |\varphi_m^{(2)}\rangle$ we find with Eq. (6.1) the expansion coefficients of such a product state

$$C_{n,m}^{\text{Product state}} = a_n b_m$$

This sets a lot of restrictions to the set of coefficients $C_{n,m}^{\text{Product state}}$. E.g.

$$C_{1,2}^{\text{Product state}}C_{2,1}^{\text{Product state}} = a_1b_2a_2b_1 = C_{1,1}^{\text{Product state}}C_{2,2}^{\text{Product state}}$$

must be satisfied. Thus states like

$$|\Psi\rangle = \frac{1}{\sqrt{2}}|\varphi_1^{(1)}\rangle \otimes |\varphi_2^{(2)}\rangle + \frac{1}{\sqrt{2}}|\varphi_2^{(1)}\rangle \otimes |\varphi_1^{(2)}\rangle$$

where all c_{nm} are zero except for $c_{12} = c_{21} = 1/\sqrt{2}$, can in principle not be written as $|\psi^{(1)}\rangle \otimes |\phi^{(2)}\rangle$. Such states are frequently called *entangled states* and their properties can be employed for quantum information processing tasks.

The most important message is: Almost all states cannot be written as product states! (Actually, there is a common misconception that all states of the product space can be written as product states.)

6.1.2 Example: Hydrogen atom as a two particle system

The hydrogen atom consists of two particles, an electron (e) and a proton (p). The two-particle state $|\Psi\rangle$ is accordingly a state of the product space between the electron space and the proton space. Now we use for both states the spatial eigenstates $|\mathbf{r}_e\rangle$, $|\mathbf{r}_p\rangle$ as a basis and the spatial representation of the product space becomes

$$\Psi(\mathbf{r}_e, \mathbf{r}_p, t) = (\langle \mathbf{r}_e | \otimes \langle \mathbf{r}_p |) | \Psi \rangle$$

This two-particle wave function $\Psi(\mathbf{r}_e, \mathbf{r}_p, t)$ has the following interpretation: $|\Psi(\mathbf{r}_e, \mathbf{r}_p, t)|^2 \Delta^3 r_e \Delta^3 r_p$ is the probability to find the electron in the volume $\Delta^3 r_e$ around \mathbf{r}_e and the proton in the volume $\Delta^3 r_p$ around \mathbf{r}_p .

Of course this requires the normalization

$$\int \mathrm{d}^3 r_e \mathrm{d}^3 r_p |\Psi(\mathbf{r}_e, \mathbf{r}_p, t)|^2 = 1.$$

Any operator acts on both particles. E.g., the operator for the total momentum reads in spatial representation $\hat{\mathbf{P}}_{\text{tot}}^{\text{SR}} = \frac{\hbar}{i} (\nabla_{r_e} + \nabla_{r_p})$, and the expectation value is

$$\langle \hat{\mathbf{P}}_{\text{tot}} \rangle = \int d^3 r_e d^3 r_p \Psi(\mathbf{r}_e, \mathbf{r}_p, t)^* \frac{\hbar}{i} (\nabla_{r_e} + \nabla_{r_p}) \Psi(\mathbf{r}_e, \mathbf{r}_p, t)$$

The Hamilton operator of the system reads

$$\hat{H}_{0}^{\mathrm{SR}} = -\frac{\hbar^{2}}{2m_{e}} \left(\frac{\partial}{\partial \mathbf{r}_{e}}\right)^{2} - \frac{\hbar^{2}}{2m_{p}} \left(\frac{\partial}{\partial \mathbf{r}_{p}}\right)^{2} - \frac{e^{2}}{4\pi\epsilon_{0}|\mathbf{r}_{e} - \mathbf{r}_{p}|}$$
(6.3)

Now we look for the solutions of the stationary Schrödinger equation

$$\hat{H}_0^{\mathrm{SR}}\Psi(\mathbf{r}_e,\mathbf{r}_p) = E\Psi(\mathbf{r}_e,\mathbf{r}_p)$$

If we introduce the relative coordinate $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_p$ and the center of mass coordinate $\mathbf{R} = (m_e \mathbf{r}_e + m_p \mathbf{r}_p)/M$ with $M = m_e + m_p$, we find:

$$\frac{\partial}{\partial \mathbf{r}_{e}}\tilde{\Psi}(\mathbf{R},\mathbf{r}) = \frac{\partial}{\partial \mathbf{R}}\tilde{\Psi}(\mathbf{R},\mathbf{r})\frac{m_{e}}{M} + \frac{\partial}{\partial \mathbf{r}}\tilde{\Psi}(\mathbf{R},\mathbf{r})$$
$$\left(\frac{\partial}{\partial \mathbf{r}_{e}}\right)^{2}\tilde{\Psi}(\mathbf{R},\mathbf{r}) = \left(\frac{\partial}{\partial \mathbf{R}}\right)^{2}\tilde{\Psi}(\mathbf{R},\mathbf{r})\left(\frac{m_{e}}{M}\right)^{2} + 2\frac{\partial}{\partial \mathbf{R}}\cdot\frac{\partial}{\partial \mathbf{r}}\tilde{\Psi}(\mathbf{R},\mathbf{r})\frac{m_{e}}{M} + \left(\frac{\partial}{\partial \mathbf{r}}\right)^{2}\tilde{\Psi}(\mathbf{R},\mathbf{r})$$
$$\left(\frac{\partial}{\partial \mathbf{r}_{p}}\right)^{2}\tilde{\Psi}(\mathbf{R},\mathbf{r}) = \left(\frac{\partial}{\partial \mathbf{R}}\right)^{2}\tilde{\Psi}(\mathbf{R},\mathbf{r})\left(\frac{m_{p}}{M}\right)^{2} - 2\frac{\partial}{\partial \mathbf{R}}\cdot\frac{\partial}{\partial \mathbf{r}}\tilde{\Psi}(\mathbf{R},\mathbf{r})\frac{m_{p}}{M} + \left(\frac{\partial}{\partial \mathbf{r}}\right)^{2}\tilde{\Psi}(\mathbf{R},\mathbf{r})$$

Together this provides

$$\hat{H}_{0}^{\mathrm{SR}}\tilde{\Psi}(\mathbf{R},\mathbf{r}) = \left(-\frac{\hbar^{2}}{2M}\left(\frac{\partial}{\partial\mathbf{R}}\right)^{2} - \frac{\hbar^{2}}{2\mu}\left(\frac{\partial}{\partial\mathbf{r}}\right)^{2} - \frac{e^{2}}{4\pi\epsilon_{0}|\mathbf{r}|}\right)\tilde{\Psi}(\mathbf{R},\mathbf{r})$$

with the reduced mass $\mu = (1/m_e + 1/m_p)^{-1}$. \hat{H}_0 is separating in the variables **R**, **r** which allows for a product ansatz for the wave-function:

$$\tilde{\Psi}(\mathbf{R},\mathbf{r}) = \frac{1}{(2\pi)^{3/2}} \mathrm{e}^{\mathrm{i}\mathbf{K}\cdot\mathbf{R}} \phi_{nlm}(\mathbf{r}) \quad \text{with} \quad \hat{H}_0 \tilde{\Psi}(\mathbf{R},\mathbf{r}) = \left(\frac{\hbar^2 \mathbf{K}^2}{2M} + E_n\right) \tilde{\Psi}(\mathbf{R},\mathbf{r})$$

Here E_n and $\phi_{nlm}(\mathbf{r})$ are the eigenvalues and eigenfunctions of Eq. (5.13) where the electron mass m_e is replaced by the reduced mass μ . The bound state as a whole, i.e. the hydrogen atom, acts as a free particle with the total mass M. Obviously, one cannot separate $\tilde{\Psi}(\mathbf{R}, \mathbf{r}) = f(\mathbf{r}_e)g(\mathbf{r}_p)$ and this is an entangled state.

In the ground state the atom is in the state $|n = 1, l = 0, m = 0, \mathbf{K} = 0\rangle$ regarding the orbital degrees of freedom. Let us now consider the spin degrees of freedom. This problem is analogous to the positronium discussed in Sec. 3.4.2, where the index p now stands for the proton instead of the positron.

The interaction between the spins can be quantified by the operator

$$\hat{V} = f(\mathbf{r}_e - \mathbf{r}_p)\hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p$$

For the ground-state we have a four-fold degeneracy if there is no spin-spin interaction. The matrix of the perturbation potential becomes diagonal if we consider the eigenstates for the total spin $\hat{\mathbf{S}} = \hat{\mathbf{S}}_e + \hat{\mathbf{S}}_p$ and we obtain the energies

$$E_{S} = -3\frac{f_{0}}{4\hbar^{2}} \qquad \text{for the singlet}$$

$$E_{T} = \frac{f_{0}}{4\hbar^{2}} \qquad \text{for the triplet}$$

with $f_0 = \int d^3 r_e \int d^3 r_p f(\mathbf{r}_e - \mathbf{r}_p) |\Psi_{n=1,l=0,m=0,K=0}(\mathbf{r}_e, \mathbf{r}_p)|^2$. This splitting by $4f_0\hbar^2/4 = 6\mu eV$ is called *hyper fine structure* and we find that the ground state with total spin S = 0 is non-degenerate. Note, that the corresponding energy difference is significantly smaller than the fine structure discussed in Sec. 3.4.3.

6.2 Identical Particles

In classical physics, particles have individual trajectories. Thus even for particles with identical properties (such as mass, charge, and further interaction strengths), one can follow the particles individually and thus it is possible to provide a labeling. Such a path does not exist in quantum mechanics and some care has to be taken when treating identical particles.

6.2.1 Symmetry of two-particle states

Like in the preceding section we start with a basis $\{|a_n\rangle\}$ of the single-particle states and any two-particle state can be written as

$$|\Psi
angle = \sum_{nm} \Psi_{nm} |a_n
angle \otimes |a_m
angle$$

Now we define the *transposition operator* \hat{T} by its action on the states of the tensor product as

$$\hat{T}|a_n\rangle\otimes|a_m\rangle=|a_m\rangle\otimes|a_n\rangle$$

Thus this transposition operator just exchanges the states of (1) and (2). Using Eq. (6.2) it can easily be shown that \hat{T} is Hermitian. As $\hat{T}^2 = 1$ its eigenvalues can only be 1 or -1 and the corresponding eigenstates are called *symmetric* or *anti-symmetric*, respectively.

Any operator acts both on the first entry of the tensor product, labeled by (1), as well as on the second entry (2). For example the kinetic energy is given by $[\hat{\mathbf{p}}^{(1)}]^2/2m + [\hat{\mathbf{p}}^{(2)}]^2/2m$ and the Coulomb interaction between the particles by $e^2/(4\pi |\hat{\mathbf{r}}^{(1)} - \hat{\mathbf{r}}^{(2)}|)$. Both operators are identical upon exchanging the indices (1) and (2) and the same holds for any physically meaningful operator \hat{A} of the two particle space, as otherwise there would be a way to distinguish both particles. Thus we find

$$\hat{T}\hat{A}|a_n\rangle \otimes |a_m\rangle = \hat{A}\hat{T}|a_n\rangle \otimes |a_m\rangle.$$

As this holds for any basis state of the ket space, any physically relevant operator satisfies

$$[\hat{A}, \hat{T}] = 0. (6.4)$$

Consequently, a common set of eigenstates exists and the eigenstates of all twoparticle operators can be classified as symmetric or anti-symmetric. This holds in particular for the Hamilton-operator determining the evolution in time. Thus, if a state is (anti-)symmetric once, it will be so forever.

Now experience with all known physical systems can be summarized in the

Symmetry-Postulate:

- Systems of particles with integer spin (bosons) are eigenstates of \hat{T} with eigenvalue 1.
- Systems of particles with half-integer spin (*fermions*) are eigenstates of of \hat{T} with eigenvalue -1.

In this context the spin is the total spin for a compound particle. Thus the ${}^{4}He$ atom is a boson and the ${}^{3}He$ atom is a fermion. Although their electron configuration is identical, they exhibit quite different low-temperature properties. As the symmetry properties determine, whether the mean occupation of a single particle level in equilibrium follows the Bose-Einstein or the Fermi-Dirac distribution, the symmetry postulate is frequently referred to as *Spin-Statistic Theorem*.¹

The basis states $|a_n, a_m\rangle = |a_n\rangle \otimes |a_m\rangle$ generally do not satisfy the symmetry postulate. However they allow for the construction of appropriate states

• Symmetrized states for bosons:

$$|a_n, a_m\rangle_S = rac{1}{\sqrt{2}\sqrt{2}^{\delta_{nm}}} (|a_n\rangle \otimes |a_m\rangle + |a_m\rangle \otimes |a_n\rangle)$$

• Anti-symmetrized states for fermions

$$|a_n, a_m\rangle_A = \frac{1}{\sqrt{2}} (|a_n\rangle \otimes |a_m\rangle - |a_m\rangle \otimes |a_n\rangle)$$

By construction we find $|a_n, a_m\rangle_A = 0$, if n = m. This provides the *Pauli-Principle*, stating that the same single-particle state (or level) must not be occupied twice by fermions.

¹This theorem can actually be derived from relativistic quantum mechanics and symmetry considerations, W. Pauli Phys. Rev. **58**, 718 (1940)

6.2.2 Permutations and extension to N-particle states^{*}

A permutation ξ is a bijective map of the set of numbers $\{1, 2, \ldots, N\}$ onto itself. A common notation is $\xi = (p_1, p_2, \ldots, p_N)$, meaning that the number *i* is mapped to p_i for $i = 1, 2, \ldots, N$, where $p_i \in \{1, 2, \ldots, N\}$ and $p_i \neq p_j$ for $i \neq j$. There are N! different permutations for a given N, which form a group with the multiplication $\xi'\xi = (p'_{p_1}, p'_{p_2}, \ldots, p'_{p_N})$ for $\xi' = (p'_1, p'_2, \ldots, p'_N)$ A transposition τ_{ij} is a special permutation, which maps the numbers $i \to j$ and $j \to i$, while all other numbers are mapped onto themselves. A well-known theorem states: Each permutation can be written as a product of either an even or an odd number of transpositions. Correspondingly, the permutation ξ is called even or odd, which is described by the function $\pi_{\xi} = \pm 1$.

Example: Name all permutations for N = 3, and provide the respective π_{ξ} .

The N! = 6 different permutations are

$$\begin{aligned} \xi_1 &= (1, 2, 3), \ \pi_{\xi_1} = 1 \\ \xi_2 &= (2, 1, 3) = \tau_{12}, \ \pi_{\xi_2} = -1 \\ \xi_3 &= (3, 2, 1) = \tau_{13}, \ \pi_{\xi_3} = -1 \\ \xi_5 &= (3, 1, 2) = \tau_{12}\tau_{13}, \ \pi_{\xi_5} = 1 \\ \xi_6 &= (2, 3, 1) = \tau_{13}\tau_{12}, \ \pi_{\xi_6} = 1 \end{aligned}$$

Note that $\tau_{13}\tau_{12} \neq \tau_{12}\tau_{13}$, i.e. the permutation operators do not commute. Furthermore, there are many ways to write $\xi_5 = \tau_{12}\tau_{13} = \tau_{13}\tau_{23} = \tau_{23}\tau_{12}$ as a product of transpositions, but all products require an even number of transpositions.

For an arbitrary number N of particles, the basis of the ket space is given by the elements

$$|a_{n_1}\rangle \otimes |a_{n_2}\rangle \otimes \ldots \otimes |a_{n_N}\rangle \tag{6.5}$$

which are ordered by the particle number. For a given permutation $\xi = (p_1, p_2, \dots, p_N)$ of the numbers $(1, 2, \dots, N)$ the *permutation operator* \hat{P}_{ξ} exchanges in the *N*particle states the counting sequence of the particles

$$\hat{P}_{\xi}|a_{n_1}\rangle \otimes |a_{n_2}\rangle \otimes \ldots \otimes |a_{n_N}\rangle = \underbrace{|a_{n_j}\rangle}_{\text{where } p_j=1} \otimes \ldots \otimes \underbrace{|a_{n_1}\rangle}_{\text{at position } p_1} \otimes \ldots \tag{6.6}$$

For the transposition τ_{ij} the corresponding operator is called \hat{T}_{ij} . Like in the two-particle case, any physically relevant *N*-particle operator satisfies $[\hat{A}, \hat{P}_{\xi}] = 0$ and the eigenstates of \hat{A} and be classified according to their properties under permutations.² The symmetry postulate reads

- Systems of particles with integer spin (*bosons*) are eigenstates of all permutation operators \hat{P}_{ξ} with eigenvalue 1.
- Systems of particles with half-integer spin (*fermions*) are eigenstates of all permutation operators \hat{P}_{ξ} with eigenvalue π_{ξ} .

Again, the basis states (6.5) allow for the construction of appropriate states

• Symmetrized states for bosons:

$$|a_{n_1}, a_{n_2}, \dots a_{n_N}\rangle_S = \frac{1}{\sqrt{N!\prod_n N_n!}} \sum_{\xi} \hat{P}_{\xi} |a_{n_1}\rangle \otimes |a_{n_2}\rangle \otimes \dots \otimes |a_{n_N}\rangle$$

where N_n denotes, how often the index *n* appears in the set $\{n_1, n_2, \ldots, n_N\}$, obviously $N = \sum_n N_n$ holds.

• Anti-symmetrized states for fermions

$$|a_{n_1}, a_{n_2}, \dots a_{n_N}\rangle_A = \frac{1}{\sqrt{N!}} \sum_{\xi} \pi_{\xi} \hat{P}_{\xi} |a_{n_1}\rangle \otimes |a_{n_2}\rangle \otimes \dots \otimes |a_{n_N}\rangle$$

which can be written as a Slater-determinant

$$|a_{n_1}, a_{n_2}, \dots a_{n_N}\rangle_A = \frac{1}{\sqrt{N!}} \begin{vmatrix} |a_{n_1}\rangle^{(1)} & |a_{n_2}\rangle^{(1)} & \dots & |a_{n_N}\rangle^{(1)} \\ |a_{n_1}\rangle^{(2)} & |a_{n_2}\rangle^{(2)} & \dots & |a_{n_N}\rangle^{(2)} \\ \vdots & \vdots & \ddots & \vdots \\ |a_{n_1}\rangle^{(N)} & |a_{n_2}\rangle^{(N)} & \dots & |a_{n_N}\rangle^{(N)} \end{vmatrix}$$

where the upper index (j) denotes the position in the tensor product.

²Note that for $N \geq 3$ some transpositions do not commute with each other, thus not all possible states can be chosen as eigenstates of all transpositions. A more thorough treatment needs concepts from representation theory.

6.3 Consequences of the Anti-Symmetrization

6.3.1 Single-particle operator

Consider the single-particle operator: $\hat{O}_{\text{SP}} = \sum_{i=1}^{N} \hat{O}^{(i)}$, which operates in the same way on all particles. Typical examples are the kinetic energy $\hat{\mathbf{p}}_{1}^{2}/2m + \hat{\mathbf{p}}_{2}^{2}/2m$, or an external potential $V(\hat{\mathbf{r}}_{1}) + V(\hat{\mathbf{r}}_{2})$.

The expectation value of an anti-symmetric two-particle state reads:

$$\begin{split} {}_{A}\langle a,b|\hat{O}_{\rm SP}|a,b\rangle_{A} =& \frac{1}{2} \left(\langle a,b|-\langle b,a| \right) \left(\hat{O}^{(1)}+\hat{O}^{(2)}\right) \left(|a,b\rangle-|b,a\rangle\right) \\ =& \frac{1}{2} \Big[\underbrace{\langle a,b|\hat{O}^{(1)}|a,b\rangle}_{=\langle a|\hat{O}|a\rangle\langle b|b\rangle=\langle a|\hat{O}|a\rangle} -\underbrace{\langle a,b|\hat{O}^{(1)}|b,a\rangle}_{=\langle a|\hat{O}|b\rangle\langle b|a\rangle=0} \\ &-\underbrace{\langle b,a|\hat{O}^{(1)}|a,b\rangle}_{=\langle b|\hat{O}|a\rangle\langle a|b\rangle=0} +\underbrace{\langle b,a|\hat{O}^{(1)}|b,a\rangle}_{=\langle b|\hat{O}|b\rangle\langle a|a\rangle=\langle b|\hat{O}|b\rangle} + \text{same terms with } \hat{O}^{(2)} \Big] \\ =& \langle a|\hat{O}|a\rangle + \langle b|\hat{O}|b\rangle = \langle a,b|\hat{O}_{\rm SP}|a,b\rangle \end{split}$$

The expectation value of a single-particle operator is not influenced by the antisymmetrization and can be evaluated by summing the properties of the individual states.

6.3.2 Two-particle operator

The two-particle operator $\hat{O}_{TP} = \hat{O}^{(1,2)}$ describes interactions between two particles. We find

$${}_{A}\langle a, b | \hat{O}^{(1,2)} | a, b \rangle_{A} = \frac{1}{2} \left(\langle a, b | - \langle b, a | \rangle \, \hat{O}^{(1,2)} \left(| a, b \rangle - | b, a \rangle \right)$$

$$= \frac{1}{2} \Big(\langle a, b | \hat{O}^{(1,2)} | a, b \rangle - \langle a, b | \hat{O}^{(1,2)} | b, a \rangle - \underbrace{\langle b, a | \hat{O}^{(1,2)} | a, b \rangle}_{= \langle a, b | \hat{O}^{(2,1)} | b, a \rangle} + \underbrace{\langle b, a | \hat{O}^{(1,2)} | b, a \rangle}_{= \langle a, b | \hat{O}^{(2,1)} | a, b \rangle} + \underbrace{\langle b, a | \hat{O}^{(1,2)} | b, a \rangle}_{= \langle a, b | \hat{O}^{(1,2)} | a, b \rangle} - \underbrace{\langle a, b | \hat{O}^{(1,2)} | b, a \rangle}_{\text{direct Term}} - \underbrace{\langle a, b | \hat{O}^{(1,2)} | b, a \rangle}_{\text{exchange-Term}}$$

In this case the anti-symmetrization provides an additional term, called *exchange* term, where the two-particle state $|a, b\rangle$ interacts with $\hat{T}|a, b\rangle$.

Consider now the electron-electron interaction

$$\hat{O}^{(1,2)} = \frac{e^2}{4\pi\epsilon_0 |\hat{\mathbf{r}}^{(1)} - \hat{\mathbf{r}}^{(2)}|}$$

and the single-particle states in spinor representation (3.56) $|a\rangle \rightarrow \varphi_a(\mathbf{r})\chi_{s_a}$ and $|b\rangle \rightarrow \varphi_b(\mathbf{r})\chi_{s_b}$, where $s_a \in \{\uparrow,\downarrow\}$ denotes the spin configuration in the column χ_{s_a} . E.g.

$$\chi_{\uparrow} = \begin{pmatrix} 1\\ 0 \end{pmatrix}$$

Then we obtain:

$${}_{A}\langle a,b|\hat{O}(1,2)|a,b\rangle_{A} = \int d^{3}r_{1} \int d^{3}r_{2} |\varphi_{a}(\mathbf{r}_{1})|^{2} \underbrace{|\chi_{s_{a}}^{(1)}|^{2}}_{=1} |\varphi_{b}(\mathbf{r}_{2})|^{2} \underbrace{|\chi_{s_{b}}^{(2)}|^{2}}_{=1} \frac{e^{2}}{4\pi\epsilon_{0}|\mathbf{r}_{i}-\mathbf{r}_{j}|} \\ -\int d^{3}r_{1} \int d^{3}r_{2} \varphi_{a}^{*}(\mathbf{r}_{1})\varphi_{b}(\mathbf{r}_{1}) \left(\left[\chi_{s_{a}}^{(1)}\right]^{\dagger} \chi_{s_{b}}^{(1)}\right) \varphi_{b}^{*}(\mathbf{r}_{2})\varphi_{a}(\mathbf{r}_{2}) \left(\left[\chi_{s_{b}}^{(2)}\right]^{\dagger} \chi_{s_{a}}^{(2)}\right) \frac{e^{2}}{4\pi\epsilon_{0}|\mathbf{r}_{i}-\mathbf{r}_{j}|}$$

The first term is the classical interaction of two charge distributions with densities $|\varphi_a(\mathbf{r}_1)|^2$ and $|\varphi_b(\mathbf{r}_2)|^2$. The second term vanishes if the spin states s_a, s_b are orthogonal. On the other hand, if the spins are aligned, i.e. $s_a = s_b$ this term (called *exchange interaction*) lowers the energy. Thus the alignment of spins is favored, which e.g. is reflected in Hund's rules.

6.4 General Treatment of Many-Body Systems

In many physical systems (atoms, molecules, solids) the behavior is dominated by the electron-electron interaction. Such systems are generally not exactly solvable. Typically a hierarchy of approaches is used to classify different features:

- Hartree-approximation: Consider product states of suitable one-particle states while satisfying the Pauli principle
- Hartree-Fock-approximation: Consider anti-symmetrized product states, providing an energy correction (Section 6.3.2) called *exchange energy* E_x .
- **Correlation effects:** The 'true' many-particle state is a linear combination of many anti-symmetrized product states. This provides further corrections in the energy called *correlation energy* E_c , which are notoriously difficult to estimate.

A common approach is density functional theory, which in practice works on the basis of a one-particle Hamiltonian with an effective potential containing terms due to the exchange and correlation energy. This allows for the treatment of rather large systems. While it can be shown that this method can provide correct properties of the ground state, the treatment of excited states is more questionable. Alternatively, Green's function techniques or the exact solution of the many-body Hamiltonian (often called configuration interaction) for few particles can be applied.