Chapter 11

Quantum states

11.1 Thermal wavelength

We consider a gas of atoms or molecules at temperature T. In Chap. 9 we defined the thermal wavelength λ_T ,

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \, ,$$

as the wavelength of a "wave packet" associated with each gas particle (atom or molecule) of mass m.

Billiard ball vs. quantum gas. At high temperatures, the gas particles can be described as billiard balls since their size in terms of λ_T is much smaller than the interparticle distance. As the temperature is lowered, the particles' wave packets begin to gain in importance \Rightarrow the quantum nature of the particles cannot be neglected! When the wave packets of the particles begin to overlap with each other, quantum effects must be taken into account.

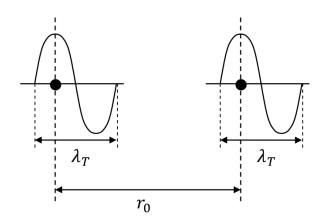
Classical regime. The system is in the *classical* regime if λ_T is much smaller than the average interparticle distance r_0 :

$$r_0 \sim \frac{1}{n^{1/3}} \; ,$$

with n being the density of particles.

The gas is in the classical regime when

$$r_0 \sim \frac{1}{n^{1/3}} \gg \lambda_T, \qquad \boxed{\lambda_T^3 n \ll 1}.$$



Quantum regime. Quantum effects become important when

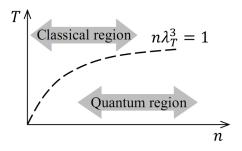
$$\lambda_T^3 n \approx 1$$
.

When this condition is fulfilled, the wave functions of different particles begin to overlap and the system has to be treated quantum mechanically.

Degeneracy temperature. The condition

$$n \left(\frac{2\pi \hbar^2}{m k_B T} \right)^{3/2} = 1$$

then defines a line in the T-n plane separating the classical from the quantum regime. It defines the degeneracy temperature T_0 as



$$k_B T_0 = \left(\frac{2\pi\hbar^2}{m}\right) n^{2/3} \ .$$

Typical degeneracy temperatures. T_0 may vary largely, depending on the physical system under study. Examples are:

$$m H_2~gas \qquad n = 2 \times 10^{19}~cm^{-3} \quad \it T_0 = 0.05~K$$
 liquid $^4{\rm He} \qquad n = 2 \times 10^{22}~cm^{-3} \quad \it T_0 = 2~K$ electrons in a metal $m \it n = 10^{22}~cm^{-3} \qquad \it T_0 = 10000~K$

We observe that, for instance, a gas can be described classically at room temperature, whereas electrons in a metal are in the extreme quantum region. Liquid Helium has a degeneracy temperature in between. At 2.17 K it makes a transition to a quantum phase that exhibits superfluidity.

11.1.1 Fundamentals of quantum statistics

Classically, the complete description of a physical system is given by

- the phase space (q, p): Γ
- the Hamilton equations of motion.

Incomplete knowledge. The solution of the equations of motion defines trajectories in the phase space, which are generally not completely known, because one cannot evaluate classically the trajectories of more than two interacting particles. One hence has to resort to statistical methods.

Indeterminism. In quantum mechanics, on top of the incomplete knowledge of the microscopic information we have the quantum mechanical *indeterminism*.

Even though the state of the system may be completely known in some special cases (viz for pure state), we still cannot predict the result of a measurement since any measurement perturbs the system. This lack of knowledge manifests itself in the statistical interpretation of the wave function and in the uncertainty relation

$$\Delta x \, \Delta p \, \sim \, h, \qquad \Delta x \, = \, \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

between the components of the space and the momentum variables, which cannot be anymore sharply measured at the same time.

classical mechanics	quantum mechanics
phase space	Hilbert space
phase space trajectories	evolution of wavefunction
$\dot{p} = -\frac{\partial H}{\partial q}, \qquad \dot{q} = \frac{\partial H}{\partial p}$	$i\hbar\frac{d\Psi}{dt} = H\Psi$

11.2 One particle states

One denotes with

$$|\Psi\rangle, \qquad |\mathbf{r}\rangle, \qquad |\mathbf{k}\rangle, \qquad |E_{\alpha}\rangle,$$

an orbital $|\Psi\rangle$.

- $-|\mathbf{r}\rangle$ corresponds to a particle which is localized at a given position \mathbf{r} in real space;
- $-|\mathbf{k}\rangle$ denotes a plane-wave state with momentum $\mathbf{p} = \hbar \mathbf{k}$;
- $-|E_{\alpha}\rangle$ is a eigenstate with an energy E_{α} , such that $\hat{H}|E_{\alpha}\rangle = E_{\alpha}|E_{\alpha}\rangle$.

Scalar products. A complex vector space such as the Hilbert space need a scalar product.

- $-\langle \Psi | \Phi \rangle$ The scalar product between two orbitals $|\Psi \rangle$ and $|\Phi \rangle$.
- $|\Phi\rangle$ 'Ket', equivalent to a vector \vec{a} in a normal vector space.
- $\langle \Psi |$ 'Bra', equivalent to the transposed and conjugated vector $[\vec{a}^*]^T$.

$$(\vec{a}|\vec{a}) = [\vec{a}^*]^T \vec{a} = \sum_i a_i^* a_i, \qquad [\vec{a}^*]^T = (a_1^*, a_2^*, a_3^*), \qquad \vec{a} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix},$$

An important scalar product is

$$\Psi(\mathbf{r}) = \langle \mathbf{r} | \Psi \rangle, \qquad \langle \mathbf{r} | \mathbf{k} \rangle = \frac{e^{i\mathbf{r} \cdot \mathbf{k}}}{\sqrt{V}}, \qquad (11.1)$$

where the first relation identifies the amplitude $\langle \mathbf{r} | \Psi \rangle$ with the wavefunction $\Psi(\mathbf{r})$.

Projection operator. The operator P_{α} ,

$$P_{\alpha} = |\alpha\rangle\langle\alpha|, \qquad P_{\alpha}|\Psi\rangle = |\alpha\rangle\langle\alpha|\Psi\rangle = \langle\alpha|\Psi\rangle|\alpha\rangle$$
 (11.2)

is a projection operator, as it projects an arbitrary state $|\Psi\rangle$ onto $|\alpha\rangle$ with an amplitude $|\alpha\rangle\Psi\rangle$ that is proportional to the cos of the respective angle.

Orthonormal states. A basis is a complete sets of orthonormal states. Important sets are

$$\hat{\mathbf{1}} = \sum_{\alpha} |E_{\alpha}\rangle\langle E_{\alpha}| = \int d^3r \, |\mathbf{r}\rangle\langle \mathbf{r}| = \int d^3k \, |\mathbf{k}\rangle\langle \mathbf{k}| , \qquad (11.3)$$

corresponding to the representation of the identity matrix $\hat{\mathbf{1}}$ by the eigenstates of \hat{H} , $\hat{\mathbf{r}}$ and of $\hat{\mathbf{p}}$ respectively. They obey the orthogonality relations

$$\langle E_{\alpha}|E_{\gamma}\rangle = \delta_{\alpha,\gamma}, \qquad \langle \mathbf{r}|\mathbf{r}'\rangle = \delta(\mathbf{r} - \mathbf{r}'), \qquad \langle \mathbf{k}|\mathbf{k}'\rangle = \delta(\mathbf{k} - \mathbf{k}').$$
 (11.4)

A basis spans the Hilbert space, being identical to the sum of projection operators that runs over a complete set of states.

Basis transformations. The representations (11.3) of the identify may be used for basis transformations, such as the *Fourier transform*

$$\Psi_{\mathbf{k}} \equiv \langle \mathbf{k} | \Psi \rangle = \int d^3 r \, \langle \mathbf{k} | \mathbf{r} \rangle \langle \mathbf{r} | \Psi \rangle = \frac{1}{\sqrt{V}} \int d^3 r \, e^{-i\mathbf{k}\cdot\mathbf{r}} \Psi(\mathbf{r}) \; ,$$

where we have used that $\langle \phi | \psi \rangle = \langle \psi | \phi \rangle^*$.

Normalization. We work exclusively with normalized states,

$$1 = \langle \Psi | \Psi \rangle = \int d^3 r \, \langle \Psi | \mathbf{r} \rangle \langle \mathbf{r} | \Psi \rangle = \int d^3 r \, |\Psi(\mathbf{r})|^2 ,$$

where $|\Psi(\mathbf{r})|^2$ is the probability to find the particle at \mathbf{r} .

11.3 The density matrix as the fundamental statistical operator

In quantum mechanics, we classify the states of a system into pure and mixed states.

11.3.1 Pure states

Consider a complete set of commuting observables. A state prepared through measuring these observables is a *pure state* and is represented by a vector $|\Psi\rangle$ in the Hilbert space.

Hermitian operators. Now, if \hat{B} is an operator associated with one of the observables in the complete set. Observables correspond to *hermitian* operators which can be expended with respect to the set of orthogonal eigenstates $|b_n\rangle$,

$$\hat{B} |b_n\rangle = b_n |b_n\rangle, \qquad \langle b_n |b_m\rangle = \delta_{nm},$$

where the b_n are the corresponding eigenvalues. The set of eigenstates of a hermitian operator span the Hilbert space. Any state $|\Psi\rangle$ can hence be written as

$$|\Psi\rangle = \sum_{n} c_n |b_n\rangle, \qquad c_n = \langle b_n | \Psi \rangle.$$

The expansion coefficients c_n are the amplitudes of $|\Psi\rangle$.

Expectation values. The expectation value is defined as $\langle B \rangle$,

$$\langle \hat{B} \rangle = \langle \Psi | \, \hat{B} | \Psi \rangle = \sum_{n} \underbrace{\langle \Psi | \, \hat{B} | b_{n} \rangle}_{b_{n} \langle \Psi | b_{n} \rangle} \underbrace{\langle b_{n} | \Psi \rangle}_{C_{n}}$$
$$= \sum_{n} b_{n} |c_{n}|^{2} .$$

One can think of the expectation value \hat{B} as the averaged result of either

- successive measurements of B done on the same system, or of
- measurements of B done simultaneously on copies of the system.

The second interpretation reminds us about the concept of the *ensemble* that we introduced in statistics.

11.3.2 Mixed states

When the information about the system is incomplete, i.e., no measurement through a complete set of commuting observables was possible, then the system is in a *mixed state*.

A mixed state cannot be represented by a Hilbert-vector. For a mixed state, we only know the probabilities that the system is in a given pure state, while the information about the relative phases is missing.

Density matrix. We have that the system can be found in pure states $|\Psi_m\rangle$, $m=1,2,\ldots$, with probabilities $0 \le P_m \le 1$, so that

$$\sum_{m} P_m = 1 ,$$

with $\langle \Psi_n | \Psi_m \rangle = \delta_{nm}$. The expectation value of an operator \hat{B} is then given by

$$\langle \hat{B} \rangle = \sum_{m} P_{m} \langle \Psi_{m} | \hat{B} | \Psi_{m} \rangle$$
.

Calculation of this expectation value includes two distinct operations:

- the evaluation of quantum mechanical expectation values $\langle \Psi_m | \hat{B} | \Psi_m \rangle$, and
- the statistical averaging over the states $|\Psi_m\rangle$ weighed by P_m , which is a consequence of the incomplete information about the system.

The central operator in quantum statistics which includes *both averages* is the density matrix operator $\hat{\rho}$:

$$\hat{\rho} = \sum_{m} P_{m} |\Psi_{m}\rangle \langle \Psi_{m}| .$$

It weights every state $|\Psi_m\rangle$ by a Boltzman factor P_m , corresponding to a supperposition of weighted projection operators $|\Psi_m\rangle \langle \Psi_m|$.

11.3.3 Properties of $\hat{\rho}$

The average value of an operator \hat{B} is given as

$$\langle \hat{B} \rangle = \operatorname{Tr}(\hat{\rho}\hat{B}) ,$$

which follows from the properties of the trace Tr() as

$$\operatorname{Tr}(\hat{\rho}\hat{B}) = \sum_{j} (\hat{\rho}\hat{B})_{jj} = \sum_{ij} \hat{\rho}_{ji}\hat{B}_{ij}$$

$$= \sum_{i,j} \left(\sum_{m} P_{m} \langle b_{j} | \Psi_{m} \rangle \langle \Psi_{m} | b_{i} \rangle \right) \langle b_{i} | \hat{B} | b_{j} \rangle$$

$$= \sum_{m,i,j} P_{m} \langle \Psi_{m} | b_{i} \rangle \langle b_{i} | \hat{B} | b_{j} \rangle \langle b_{j} | \Psi_{m} \rangle$$

$$= \sum_{m} P_{m} \langle \Psi_{m} | \left(\sum_{i} |b_{i} \rangle \langle b_{i}| \right) \hat{B} \left(\sum_{j} |b_{j} \rangle \langle b_{j}| \right) |\Psi_{m} \rangle$$

$$= \sum_{m} P_{m} \langle \Psi_{m} | \hat{B} | \Psi_{m} \rangle = \langle \hat{B} \rangle.$$

Hermitian operators have real eigenvalues. The density matrix is hermitian,

$$\hat{\rho} = \hat{\rho}^{\dagger}$$
.

since the projector $|\Psi_m\rangle \langle \Psi_m|$ is hermitian. The eigenvalues of $\hat{\rho}$ are therefore real. **Normalization.** The trace of the density operator is normalized,

$$\operatorname{Tr}\hat{\rho} \equiv \sum_{n} \langle \Psi_{n} | \hat{\rho} | \Psi_{n} \rangle = \sum_{m,n} P_{m} \langle \Psi_{n} | \Psi_{m} \rangle \langle \Psi_{m} | \Psi_{n} \rangle = \sum_{m} P_{m} = 1$$

because the probability distribution P_m is normalized per definition.

Non negativity. For a given state $|\varphi\rangle$ one has

$$\langle \varphi | \hat{\rho} | \varphi \rangle = \sum_{m} P_{m} |\langle \varphi | \Psi_{m} \rangle|^{2} \geq 0 , \qquad P_{m} \geq 0 .$$

The density matrix $\hat{\rho}$ is consequently non-negative.

Density matrix of pure states. Pure states $|\Psi\rangle$ are be represented as

$$\hat{\rho}_{\Psi} = |\Psi\rangle\langle\Psi|$$
 .

The density matrix reduces consequently to projection matrix.

Powers of the density matrix. The square of $\hat{\rho}$ is

$$\hat{\rho}^2 = \sum_m P_m^2 |\Psi_m\rangle \langle \Psi_m|, \qquad \operatorname{Tr} \hat{\rho}^2 = \sum_m P_m^2,$$

From $0 \le P_m \le 1$ it then follows that

$$\sum_{m} P_m^2 \le \sum_{m} P_m = 1 .$$

Powers of $\hat{\rho}$ are therefore not normalized.

Time evolution. The time evolution of $\hat{\rho}$ is given in the *Schrödinger picture* with $i\hbar|\dot{\psi}\rangle = H|\psi\rangle$ and $\langle\dot{\psi}|(-i\hbar) = \langle\psi|H|$ by

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = \sum_{m} P_m \Big(|\dot{\Psi}_m\rangle \langle \Psi_m| + |\Psi_m\rangle \langle \dot{\Psi}_m| \Big) = [H, \hat{\rho}],$$

which is the quantum mechanical analogue of the Liouville equation.

Thermal equilibrium. Thermal equilibrium is reached when the expectation value of a macroscopic observable B,

$$\langle \hat{B} \rangle = \text{Tr}(\hat{\rho}(t)\hat{B})$$
,

does not change any with respect to time. This is only possible if $\hat{\rho}(t)$ is also time independent,

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{1}{i\hbar} \left[\hat{\rho}, H \right] = 0 ,$$

which implies that $\hat{\rho}$ is a conserved quantity. This is in particular the case if $\hat{\rho} = \hat{\rho}(H)$.

11.3.4 Correspondence principle

We recall the properties of a statistical ensemble.

- A statistical ensemble is composed of an infinite set of exact copies of the real system.
- The microscopic details of the individual states are not fully known, which means that the system is in a mixed state.
- Each member of the ensemble is in a possible state $|\Psi_m\rangle$.
- The ensemble is described by an *incoherent* set of states as the members of the ensemble don't interact with each other and their states don't interfere with each other.

Correspondence principle. It is a times useful to work with *correspondence principle*, which relates classical and quantum physics.

	Classical	QM
1	Phase space function $B(q,p)$	Operator \hat{B}
2	Probability distribution function $\rho(q,p)$	Statistical operator $\hat{\rho}$
3	Poisson brackets $[B,G]_L = \sum_j \left(\frac{\partial B}{\partial q_j} \cdot \frac{\partial G}{\partial p_j} - \frac{\partial G}{\partial q_j} \cdot \frac{\partial B}{\partial p_j} \right)$	Commutators $\frac{1}{i\hbar} \left[\hat{B}, \hat{G} \right] = \frac{1}{i\hbar} \left(\hat{B}\hat{G} - \hat{G}\hat{B} \right)$
4	Phase space integration $\frac{1}{h^{3N}N!} \int d^{3N}q \ d^{3N}p \dots$	Trace $\operatorname{Tr}(\ldots)$
5	Ensemble in equilibrium (stationary state):	
	$[\rho, H]_L = 0$	$[\hat{\rho}, H]_{-} = 0$
Statistical average of an observable B	$\langle B \rangle = \frac{1}{h^{3N} N!} \int d^{3N} q \ d^{3N} p \ \rho(q, p) B(q, p)$ $1 = \frac{1}{h^{3N} N!} \int d^{3N} q \ d^{3N} p \ \rho(q, p)$	$<\hat{B}>=\mathrm{Tr}(\hat{\rho}\hat{B})$ $1=\mathrm{Tr}\hat{\rho}$
Equation of motion	Liouville equation: $\frac{\partial \rho}{\partial t} = [H, \rho]_L$ $H : \text{ Hamilton function}$	$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} \left[\hat{H}, \hat{\rho} \right]_{-}$ $\hat{H}: \text{ Hamilton operator}$

11.4 Statistics of identical particles

Nothing happens if there are no particles around. We define with

$$|\phi\rangle = a_{\phi}^{\dagger}|0\rangle \qquad a_{\phi}|\phi\rangle = |0\rangle \langle \phi| = \langle 0|a_{\phi} \qquad a_{\phi}|0\rangle = 0$$

$$(11.5)$$

the creation operator a_{ϕ}^{\dagger} , the annihilation operator a_{ϕ} and the vacuum $|0\rangle$.

Spin-statistic theorem. Pauli's spin-statistics theorem states that there are two types of elementary particles.

BOSONS Elementary particle with an integer spin S=0,1,... are bosons. Their wavefunction is symmetric.

FERMIONS Elementary particle with an integer spin S=1/2,3/2,... are fermions. Their wavefunction is anti symmetric.

Symmetric and anti-symmetric refers here with respect to the exchange of particles.

States with more than one particle. The spin statistic theorem translates directly into exchange relation for two- and more particle states in the sense that

$$a_{\phi}^{\dagger} a_{\psi}^{\dagger} |0\rangle = a_{\psi}^{\dagger} a_{\phi}^{\dagger} |0\rangle, \qquad c_{\phi}^{\dagger} c_{\psi}^{\dagger} |0\rangle = -c_{\psi}^{\dagger} c_{\phi}^{\dagger} |0\rangle , \qquad (11.6)$$

where we have denoted the creation operators for bosons and fermions respectively with a_{ϕ}^{\dagger} and c_{ψ}^{\dagger} .

Commutator. The interchange of creation and/or annihilation operators can be formalized. One defines with

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}, \qquad [\hat{A}, \hat{B}]_{+} = \hat{A}\hat{B} + \hat{B}\hat{A}$$
 (11.7)

the commutator $[\hat{A}, \hat{B}]$ and the anti-commutator $[\hat{A}, \hat{B}]_+$ of two operators \hat{A} and \hat{B} .

Exchange relations. The spin statistics theorem takes its mathematical formulation via the commutation relations

$$\begin{bmatrix}
a_{\psi}, a_{\phi} \end{bmatrix} = \begin{bmatrix} a_{\psi}^{\dagger}, a_{\phi}^{\dagger} \end{bmatrix} = 0 \\
\begin{bmatrix} a_{\psi}, a_{\phi}^{\dagger} \end{bmatrix} = \delta_{\psi, \phi} \\
\end{aligned}$$
bosons

for bosons and respectively for fermions:

$$\begin{bmatrix}
[c_{\psi}, c_{\phi}]_{+} &= [c_{\psi}^{\dagger}, c_{\phi}^{\dagger}]_{+} &= 0 \\
[c_{\psi}, c_{\phi}^{\dagger}]_{+} &= \delta_{\psi, \phi}
\end{bmatrix}$$
Fermions

Transformation of creation operators. The representations (11.3) of the identity matrix $\hat{\mathbf{1}}$ serves as the basis for transforming creation and annihilation operators. As an example we consider

$$|\Psi\rangle = \int d^3r \, |\mathbf{r}\rangle\langle\mathbf{r}|\Psi\rangle, \qquad c_{\psi}^{\dagger} = \int d^3r \, \langle\mathbf{r}|\Psi\rangle \, c_{\mathbf{r}}^{\dagger} \,, \qquad (11.10)$$

where we have used $|\Psi\rangle = c_{\Psi}^{\dagger}|0\rangle$ and $|\mathbf{r}\rangle = c_{\mathbf{r}}^{\dagger}|0\rangle$.

Plane waves. The relation (11.10) becomes

$$c_{\mathbf{k}}^{\dagger} = \int d^3 r \, \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \, c_{\mathbf{r}}^{\dagger} \tag{11.11}$$

for the case that $|\Psi\rangle = |\mathbf{k}\rangle$. We have used here the amplitude (11.1) of a plane wave.

Particle number operator. The operator

$$\hat{n}_{\psi} = a_{\psi}^{\dagger} a_{\psi}, \qquad \hat{n}_{\psi} = c_{\psi}^{\dagger} c_{\psi} \tag{11.12}$$

measures the number of particle in the orbital ψ , both for Bosons and for Fermions.

One particle states. We verify (11.12) for a bosonic one-particle state $|\psi\rangle = a_{\psi}^{\dagger}|0\rangle$:

$$\langle \psi | \hat{n}_{\phi} | \psi \rangle = \langle 0 | a_{\psi} a_{\phi}^{\dagger} a_{\phi} a_{\psi}^{\dagger} | 0 \rangle, \qquad a_{\phi} a_{\psi}^{\dagger} = \delta_{\psi,\phi} + a_{\psi}^{\dagger} a_{\phi}$$

$$= \delta_{\psi,\phi} \underbrace{\langle 0 | a_{\psi} a_{\phi}^{\dagger} | 0 \rangle}_{=\langle \psi | \phi \rangle} + \langle 0 | a_{\psi} a_{\phi}^{\dagger} a_{\psi}^{\dagger} \underbrace{a_{\phi} | 0 \rangle}_{=0} = \delta_{\psi,\phi} . \qquad (11.13)$$

There is no particle of type ϕ in $|\psi\rangle$, but one of type ψ .

Commutation relation. Considering $\phi = \psi$ we note that (11.13) is equivalent to

$$\hat{n}_\psi a_\psi^\dagger \,=\, a_\psi^\dagger a_\psi^{} a_\psi^\dagger \,=\, a_\psi^\dagger (1 + a_\psi^\dagger a_\psi^{}) \,=\, a_\psi^\dagger (1 + \hat{n}_\psi^{}) \;, \label{eq:normalization}$$

which leads to the commutation relations

$$[\hat{n}_{\psi}, a_{\psi}^{\dagger}] = a_{\psi}^{\dagger}, \qquad \boxed{\langle a_{\psi}^{\dagger} a_{\psi} \rangle = 0, 1, 2 \dots}$$
bosons
$$(11.14)$$

where the last equation is proven by considering n-times the commutator $[\hat{n}_{\psi}, a_{\psi}^{\dagger}]$ in a state $(a_{\psi}^{\dagger})^n |0\rangle$, that is in an oribital occupied n-fold.

Fermi principle. For Fermions we note that (11.6) reduces for $\psi = \phi$

$$c_{\psi}^{\dagger}c_{\psi}^{\dagger}|0\rangle = -c_{\psi}^{\dagger}c_{\psi}^{\dagger}|0\rangle, \qquad c_{\psi}^{\dagger}c_{\psi}^{\dagger}|0\rangle = 0$$
fermions (11.15)

No more than one Fermion can occupy a given orbital ψ .

11.4.1 Slater determinant

As an example we evaluate the amplitude to find two fermions in real space at \mathbf{r}_1 and \mathbf{r}_2 . The fermions occupy the orbitals $|\psi\rangle$ and $|\phi\rangle$. We then need the amplitude

$$\langle \mathbf{r_1}, \mathbf{r_2} | \psi, \phi \rangle, \qquad \langle \mathbf{r_1}, \mathbf{r_2} | = \langle 0 | c_{\mathbf{r_1}} c_{\mathbf{r_2}}, \qquad | \psi, \phi \rangle = c_{\psi}^{\dagger} c_{\phi}^{\dagger} | 0 \rangle.$$
 (11.16)

Using (11.10) the two-particle amplitude (11.16) takes the form

$$\langle \mathbf{r_1}, \mathbf{r_2} | \psi, \phi \rangle = \int d^3 r \, d^3 r' \, \langle \mathbf{r} | \psi \rangle \langle \mathbf{r}' | \phi \rangle \, \langle 0 | c_{\mathbf{r_1}} c_{\mathbf{r_2}} c_{\mathbf{r}'}^{\dagger} c_{\mathbf{r}'}^{\dagger} | 0 \rangle . \tag{11.17}$$

Commutating through. Expectation values like the ones showing up on the right-hand side of (11.17) are evaluated via the repeated application of the commutation relations, such as

$$c_{\mathbf{r}_{1}}c_{\mathbf{r}_{2}}c_{\mathbf{r}}^{\dagger}c_{\mathbf{r}'}^{\dagger} = c_{\mathbf{r}_{1}}\left[\delta(\mathbf{r} - \mathbf{r}_{2}) - c_{\mathbf{r}}^{\dagger}c_{\mathbf{r}_{2}}\right]c_{\mathbf{r}'}^{\dagger}$$

$$= \delta(\mathbf{r} - \mathbf{r}_{2})\left[c_{\mathbf{r}_{1}}c_{\mathbf{r}'}^{\dagger}\right] - \left[c_{\mathbf{r}_{1}}c_{\mathbf{r}}^{\dagger}\right]\left[c_{\mathbf{r}_{2}}c_{\mathbf{r}'}^{\dagger}\right]$$
(11.18)

where we adapted (11.9) to the case of continuous states.

- $-c_{\mathbf{x}}|0\rangle = 0$ for all \mathbf{x} implies that terms where a destruction operator is commutated fully to the right will vanish when the expectation value with the vacuum $|0\rangle$ is taken.
- Idem for $\langle 0|c_{\mathbf{x}}^{\dagger}=0.$

Using the commutation relations like $c_{\mathbf{r_1}}c_{\mathbf{r'}}^{\dagger} = \delta(\mathbf{r_1} - \mathbf{r'}) - c_{\mathbf{r'}}^{\dagger}c_{\mathbf{r_1}}$, for the three remaining pairs of destruction/creation operators in (11.18) we then find

$$\langle 0|c_{\mathbf{r}_1}c_{\mathbf{r}_2}c_{\mathbf{r}}^{\dagger}c_{\mathbf{r}'}^{\dagger}|0\rangle = \delta(\mathbf{r} - \mathbf{r}_2)\delta(\mathbf{r}' - \mathbf{r}_1) - \delta(\mathbf{r} - \mathbf{r}_1)\delta(\mathbf{r}' - \mathbf{r}_2) . \tag{11.19}$$

Slater determinant. With (11.10) and (11.17) we find

$$\begin{vmatrix} \langle \mathbf{r_1}, \mathbf{r_2} | \psi, \phi \rangle = \langle \mathbf{r_2} | \psi \rangle \langle \mathbf{r_1} | \phi \rangle - \langle \mathbf{r_1} | \psi \rangle \langle \mathbf{r_2} | \phi \rangle = \begin{vmatrix} \langle \mathbf{r_1} | \psi \rangle & \langle \mathbf{r_2} | \psi \rangle \\ \langle \mathbf{r_1} | \phi \rangle & \langle \mathbf{r_2} | \phi \rangle \end{vmatrix} ,$$

where the determinant on the right-hand side is denote *Slater determinant*. The amplitude to find two fermions at the same site $\mathbf{r}_1 = \mathbf{r}_2$ vanishes as a consequence of the antisymmetry of the wavefunction.