Kapitel 3

Fermions and bosons

We now turn to the quantum statistical description of many-particle systems. The indistinguishability of microparticles leads to a number of far-reaching consequences for the behavior of particle ensembles. Among them are the symmetry properties of the wave function. As we will see there exist only two different symmetries leading to either Bose or Fermi-Dirac statistics.

Consider a single nonrelativistic quantum particle described by the hamiltonian $\hat{h}$. The stationary eigenvalue problem is given by the Schrödinger equation

$$\hat{h}|\phi_i\rangle = \epsilon_i|\phi_i\rangle, \qquad i = 1, 2, \dots , \tag{3.1}$$

where the eigenvalues of the hamiltonian are ordered, $\epsilon_1 < \epsilon_2 < \epsilon_3 \dots$. The associated single-particle orbitals ϕ_i form a complete orthonormal set of states in the single-particle Hilbert space[1]

$$\begin{aligned} \langle\phi_i|\phi_j\rangle &= \delta_{i,j}, \\ \sum_{i=1}^{\infty} |\phi_i\rangle\langle\phi_i| &= 1. \end{aligned} \tag{3.2}$$

3.1 Spin statistics theorem

We now consider the quantum mechanical state $|\Psi\rangle$ of N identical particles which is characterized by a set of N quantum numbers[2] $j_1, j_2, ..., j_N$, meaning that particle i is in single-particle state $|\phi_{j_i}\rangle$. The states $|\Psi\rangle$ are elements of the N-particle Hilbert space which we define as the direct product of single-particle

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[1] The eigenvalues are assumed to be non-degenerate. Also, the extension to the case of a continuous basis is straightforward.

[2] The quantum numbers comprise all orbital and spin quantum numbers of a single particle.

Abbildung 3.1: Example of the occupation of single-particle orbitals by 3 particles. Exchange of identical particles (right) cannot change the measurable physical properties, such as the occupation probability.

Hilbert spaces, $\mathcal{H}_N = \mathcal{H}_1 \otimes \mathcal{H}_1 \otimes \mathcal{H}_1 \otimes \dots$ (N factors), and are eigenstates of the total hamiltonian $\hat{H}$,

$$\hat{H}|\Psi_{\{j\}}\rangle = E_{\{j\}}|\Psi_{\{j\}}\rangle, \qquad \{j\} = \{j_1, j_2, \dots\}\,. \tag{3.3}$$

The explicit structure of the $N-$particle states is not important now and will be discussed later[3].

Since the particles are assumed indistinguishable it is clear that all physical observables cannot depend upon which of the particles occupies which single particle state, as long as all occupied orbitals, i.e. the set j, remain unchainged. In other words, exchanging two particles k and l (exchanging their orbitals, $j_k \leftrightarrow j_l$) in the state $|\Psi\rangle$ may not change the probability density, cf. Fig. 3.1. The mathematical formulation of this statement is based on the permutation operator P_{kl} with the action

$$\begin{aligned} P_{kl}|\Psi_{\{j\}}\rangle &= P_{kl}|\Psi_{j_1,\dots,j_k,\dots j_l,\dots,j_N}\rangle = \\ &= |\Psi_{j_1,\dots,j_l,\dots j_k,\dots,j_N}\rangle \equiv |\Psi'_{\{j\}}\rangle, \qquad \forall k,l = 1,\dots N, \end{aligned} \tag{3.4}$$

where we have to require

$$\langle\Psi'_{\{j\}}|\Psi'_{\{j\}}\rangle = \langle\Psi_{\{j\}}|\Psi_{\{j\}}\rangle. \tag{3.5}$$

Indistinguishability of particles requires $P_{kl}\hat{H} = \hat{H}$ and $[P_{kl}, \hat{H}] = 0$, i.e. P_{kl} and $\hat{H}$ have common eigenstates. This means P_{kl} obeys the eigenvalue problem

$$P_{kl}|\Psi_{\{j\}}\rangle = \lambda_{kl}|\Psi_{\{j\}}\rangle = |\Psi'_{\{j\}}\rangle. \tag{3.6}$$

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[3] Recall that, in this section, we assume that the particles do not interact with each other. The generalization to interacting particles will be discussed in Sec. 3.2.5.

Obviously, $P_{kl}^\dagger = P_{kl}$, so the eigenvalue λ_{kl} is real. Then, from Eqs. (3.5) and (3.6) immediately follows

$$\lambda_{kl}^2 = \lambda^2 = 1, \qquad \forall k, l = 1, \dots N, \tag{3.7}$$

with the two possible solutions: $\lambda = 1$ and $\lambda = -1$. From Eq. (3.6) it follows that, for $\lambda = 1$, the wave function $|\Psi\rangle$ is symmetric under particle exchange whereas, for $\lambda = -1$, it changes sign (i.e., it is "anti-symmetric").

This result was obtained for an arbitrary pair of particles, so we may expect that it is straightforwardly extended to systems with more than two particles. Experience shows that, in nature, there exist only two classes of microparticles – one which has a totally symmetric wave function with respect to exchange of any particle pair whereas, for the other, the wave function is antisymmetric. The first case describes particles with Bose-Einstein statistics ("bosons") and the second, particles obeying Fermi-Dirac statistics ("fermions")[4].

The one-to-one correspondence of (anti-)symmetric states with bosons (fermions) is the content of the spin-statistics theorem. It was first proven by Fierz [Fie39] and Pauli [Pau40] within relativistic quantum field theory. Requirements include 1.) Lorentz invariance and relativistic causality, 2.) positivity of the energies of all particles and 3.) positive definiteness of the norm of all states.

3.2 Symmetric and antisymmetric N-particle wave functions

We now explicitly construct the N-particle wave function of a system of many fermions or bosons.

Case of $N = 2$. For two particles occupying the orbitals $|\phi_{j_1}\rangle$ and $|\phi_{j_2}\rangle$, respectively, there are two possible wave functions: $|\Psi_{j_1,j_2}\rangle$ and $|\Psi_{j_2,j_1}\rangle$ which follow from one another by applying the permutation operator P_{12}. Since both wave functions represent the same physical state it is reasonable to eliminate this ambiguity by constructing a new wave function as a suitable linear combination of the two,

$$|\Psi_{j_1,j_2}\rangle^{\pm} \quad = \quad C_{12}\left\{|\Psi_{j_1,j_2}\rangle + A_{12}P_{12}|\Psi_{j_1,j_2}\rangle\right\}, \tag{3.8}$$

with an arbitrary complex coefficient A_{12}. Using the eigenvalue property of the permutation operator, Eq. (3.6), we require that this wave function has the

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[4] Fictitious systems with mixed statistics have been investigated by various authors, e.g. [MG64, MG65] and obey "parastatistics". For a text book discussion, see Ref. [Sch08], p. 6.

proper symmetry,

$$P_{12}|\Psi_{j_1,j_2}\rangle^{\pm} = \pm|\Psi_{j_1,j_2}\rangle^{\pm}\,, \tag{3.9}$$

which follows from the linearity of $|\Psi\rangle^{\pm}$ in the eigenstates of P. The explicit form of the coefficients in Eq. (3.8) is obtained by acting on this equation with the permutation operator and equating this to $\pm|\Psi_{j_1,j_2}\rangle^{\pm}$, according to Eq. (3.9), and using $P_{12}^2 = \hat{1}$,

$$\begin{aligned} P_{12}|\Psi_{j_1,j_2}\rangle^{\pm} &= C_{12}\left\{|\Psi_{j_2,j_1}\rangle + A_{12}P_{12}^2|\Psi_{j_1,j_2}\rangle\right\} = \\ &= C_{12}\left\{\pm A_{12}|\Psi_{j_2,j_1}\rangle \pm |\Psi_{j_1,j_2}\rangle\right\}, \end{aligned}$$

which leads to the requirement $A_{12} = \lambda$, whereas normalization of $|\Psi_{j_1,j_2}\rangle^{\pm}$ yields $C_{12} = 1/\sqrt{2}$. The final result is

$$\boxed{|\Psi_{j_1,j_2}\rangle^{\pm} = \frac{1}{\sqrt{2}}\left\{|\Psi_{j_1,j_2}\rangle \pm P_{12}|\Psi_{j_1,j_2}\rangle\right\} \equiv \Lambda_{12}^{\pm}|\Psi_{j_1,j_2}\rangle} \tag{3.10}$$

where,

$$\Lambda_{12}^{\pm} = \frac{1}{\sqrt{2}}\{1 \pm P_{12}\}, \tag{3.11}$$

denotes the (anti-)symmetrization operator of two particles which is a linear combination of the identity operator and the pair permutation operator.

Case of $N = 3$. The extension of this result to 3 fermions or bosons is straightforward. For 3 particles $(1,2,3)$ there exist $6 = 3!$ permutations: three pair permutations, $(2,1,3), (3,2,1), (1,3,2)$, that are obtained by acting with the permutation operators P_{12}, P_{13}, P_{23}, respectively on the initial configuration. Further, there are two permutations involving all three particles, i.e. $(3,1,2)$ and $(2,3,1)$, which are obtained by applying the operators $P_{13}P_{12}$ and $P_{23}P_{12}$, respectively. Thus, the three-particle (anti-)symmetrization operator has the form

$$\Lambda_{123}^{\pm} = \frac{1}{\sqrt{3!}}\{1 \pm P_{12} \pm P_{13} \pm P_{23} + P_{13}P_{12} + P_{23}P_{12}\}, \tag{3.12}$$

where we took into account the necessary sign change in the case of fermions resulting for any pair permutation.

General case. This result is generalized to N particles where there exists a total of $N!$ permutations, according to[5]

$$|\Psi_{\{j\}}\rangle^{\pm} = \Lambda_{1\ldots N}^{\pm}|\Psi_{\{j\}}\rangle, \tag{3.13}$$

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[5] This result applies only to fermions. For bosons the prefactor has to be corrected, cf. Eq. (3.25).

with the definition of the (anti-)symmetrization operator of N particles,

$$\boxed{\Lambda^{\pm}_{1\dots N} = \frac{1}{\sqrt{N!}} \sum_{P \epsilon S_N} \mathrm{sign}(P) \hat{P}} \tag{3.14}$$

where the sum is over all possible permutations $\hat{P}$ which are elements of the permutation group S_N. Each permutation P has the parity, $\mathrm{sign}(P) = (\pm 1)^{N_p}$, which is equal to the number N_p of successive pair permuations into which $\hat{P}$ can be decomposed (cf. the example $N = 3$ above). Below we will construct the (anti-)symmetric state $|\Psi_{\{j\}}\rangle^{\pm}$ explicitly. But before this we consider an alternative and very efficient notation which is based on the occupation number formalism.

The properties of the (anti-)symmetrization operators $\Lambda^{\pm}_{1\dots N}$ are analyzed in Problem 1, see Sec. 3.9.

3.2.1 Occupation number representation

The original N-particle state $|\Psi_{\{j\}}\rangle$ contained clear information about which particle occupies which state. Of course, this information is unphysical, as it is in conflict with the indistinguishability of particles. With the construction of the symmetric or anti-symmetric N-particle state, $|\Psi_{\{j\}}\rangle^{\pm}$, this information about the identity of particles is eliminated, and the only information which is retained is *how many particles*, n_p, occupy the single-particle orbital $|\phi_p\rangle$. We thus may use a different notation for the state $|\Psi_{\{j\}}\rangle^{\pm}$ in terms of the *occupation numbers* n_p of the single-particle orbitals,

$$|\Psi_{\{j\}}\rangle^{\pm} = |n_1 n_2 \dots\rangle \equiv |\{n\}\rangle, \qquad n_p = 0, 1, 2, \dots, \qquad p = 1, 2, \dots \tag{3.15}$$

Here $\{n\}$ denotes the total set of occupation numbers of all single-particle orbitals. Since this is the complete information about the N-particle system, these states form a complete system that is orthonormal by construction of the (anti-)symmetrization operators,

$$\begin{aligned} \langle\{n\}|\{n'\}\rangle &= \delta_{\{n\},\{n'\}} \equiv \delta_{n_1,n_1'} \delta_{n_2,n_2'} \dots \\ \sum_{\{n\}} |\{n\}\rangle\langle\{n\}| &= 1. \end{aligned} \tag{3.16}$$

The attractive feature of this representation is that it is equally applicable to fermions and bosons. The only difference between the two lies in the allowed values of the occupation numbers, as we will see in the next two sections.

3.2.2 Fock space

In Sec. 3.1 we have introduced the N-particle Hilbert space $\mathcal{H}_N$. In the following we will need either totally symmetric or totally anti-symmetric states which form the sub-spaces $\mathcal{H}_N^+$ and $\mathcal{H}_N^-$ of the Hilbert space. Furthermore, below we will develop the formalism of second quantization by defining creation and annihilation operators acting on symmetric or anti-symmetric states. Obviously, the action of these operators will give rise to a state with $N+1$ or $N-1$ particles. Thus, we have to introduce, in addition, a more general space containing states with different particle numbers: We define the symmetric (anti-symmetric) *Fock space* $\mathcal{F}^\pm$ as the direct sum of symmetric (anti-symmetric) Hilbert spaces $\mathcal{H}_N^\pm$ with particle numbers $N = 0, 1, 2, \dots,$

$$\begin{aligned} \mathcal{F}^+ &= \mathcal{H}_0 \cup \mathcal{H}_1^+ \cup \mathcal{H}_2^+ \cup \dots, \\ \mathcal{F}^- &= \mathcal{H}_0 \cup \mathcal{H}_1^- \cup \mathcal{H}_2^- \cup \dots. \end{aligned} \tag{3.17}$$

Here, we included the *vacuum state* $|0\rangle = |0, 0, \dots\rangle$ which is the state without particles which belongs to both Fock spaces.

3.2.3 Non-interacting many-fermion wave function

Pauli principle: Let us return to the case of two particles, Eq. (3.10), and consider the case $j_1 = j_2$. Due to the minus sign in front of P_{12}, we immediately conclude that $|\Psi_{j_1,j_1}\rangle^- \equiv 0$. This state is not normalizable and thus cannot be physically realized. In other words, two fermions cannot occupy the same single-particle orbital – this is the *Pauli principle* stating that two fermions cannot occupy an identical single-particle quantum state, which has far-reaching consequences for the behavior of fermions.

We now construct the explicit form of the anti-symmetric wave function. This is particularly simple if the particles are non-interacting. Then, the total hamiltonian is additive[6],

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_i, \tag{3.18}$$

and all hamiltonians commute, $[\hat{h}_i, \hat{h}_j] = 0$, for all i and j. Then all particles have common eigenstates, and the total wave function (prior to anti-symmetrization) has the form of a product

$$\boxed{|\Psi_{\{j\}}\rangle = |\Psi_{j_1,j_2,\dots j_N}\rangle = |\phi_{j_1}(1)\rangle|\phi_{j_2}(2)\rangle \dots |\phi_{j_N}(N)\rangle}$$

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[6] This is an example of an observable of single-particle type which will be discussed more in detail in Sec. 3.3.1.

where the argument of the orbitals denotes the number (index) of the particle that occupies this orbital. As we have just seen, for fermions, all orbitals have to be different. Now, the anti-symmetrization of this state can be performed immediately, by applying the operator $\Lambda^-_{1\dots N}$ given by Eq. (3.14). For two particles, we obtain

$$\begin{aligned} |\Psi_{j_1,j_2}\rangle^- &= \frac{1}{\sqrt{2!}}\left\{|\phi_{j_1}(1)\rangle|\phi_{j_2}(2)\rangle - |\phi_{j_1}(2)\rangle|\phi_{j_2}(1)\rangle\right\} = \\ &= |0,0,\dots,1,\dots,1,\dots\rangle. \end{aligned} \tag{3.19}$$

In the last line, we used the occupation number representation, which has everywhere zeroes (unoccupied orbitals) except for the two orbitals with numbers j_1 and j_2. Obviously, the combination of orbitals in the first line can be written as a determinant which allows for a compact notation of the general wave function of N fermions as a *Slater determinant*,

$$\begin{aligned} |\Psi_{j_1,j_2,\dots j_N}\rangle^- &= \frac{1}{\sqrt{N!}}\begin{vmatrix} |\phi_{j_1}(1)\rangle & |\phi_{j_1}(2)\rangle & \dots & |\phi_{j_1}(N)\rangle \\ |\phi_{j_2}(1)\rangle & |\phi_{j_2}(2)\rangle & \dots & |\phi_{j_2}(N)\rangle \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix} = \\ &= |0,0,\dots,1,\dots,1,\dots,1,\dots,1,\dots\rangle. \end{aligned} \tag{3.20}$$

In the last line, the 1's are at the positions of the occupied orbitals. This becomes obvious if the system is in the ground state, then the N energetically lowest orbitals are occupied, $j_1 = 1, j_2 = 2, \dots j_N = N$, and the state has the simple notation $|1,1,\dots 1,0,0\dots\rangle$ with N subsequent 1's. Obviously, the anti-symmetric wave function is normalized to unity.

As discussed in Sec. 3.2.1, the (anti-)symmetric states form an orthonormal basis in Fock space. For fermions, the restriction of the occupation numbers leads to a slight modification of the completeness relation which we, therefore, repeat:

$$\begin{aligned} \langle\{n\}|\{n'\}\rangle &= \delta_{n_1,n'_1}\delta_{n_2,n'_2}\dots, \\ \sum_{n_1=0}^{1}\sum_{n_2=0}^{1}\dots|\{n\}\rangle\langle\{n\}| &= 1. \end{aligned} \tag{3.21}$$

3.2.4 Non-interacting many-boson wave function

The case of bosons is analyzed analogously. Considering again the two-particle case

$$\begin{aligned} |\Psi_{j_1,j_2}\rangle^+ &= \frac{1}{\sqrt{2!}}\left\{|\phi_{j_1}(1)\rangle|\phi_{j_2}(2)\rangle + |\phi_{j_1}(2)\rangle|\phi_{j_2}(1)\rangle\right\} = \\ &= |0,0,\dots,1,\dots,1,\dots\rangle, \end{aligned} \tag{3.22}$$

the main difference to the fermions is the plus sign. Thus, this wave function is not represented by a determinant, but this combination of products with positive sign is called a *permanent*.

The plus sign in the wave function (3.22) has the immediate consequence that the situation $j_1 = j_2$ now leads to a physical state, i.e., for bosons, there is no restriction on the occupation numbers of individual orbitals, except for their normalization

$$\sum_{p=1}^{\infty} n_p = N, \qquad n_p = 0, 1, 2, \dots N, \quad \forall p. \tag{3.23}$$

Thus, the two single-particle orbitals $|\phi_{j_1}\rangle$ and $|\phi_{j_2}\rangle$ occuring in Eq. (3.22) can accomodate an arbitrary number of bosons. If, for example, the two particles are both in the state $|\phi_j\rangle$, the symmetric wave function becomes

$$\begin{aligned} |\Psi_{j,j}\rangle^+ &= |0, 0, \dots, 2, \dots\rangle = \\ &= C(n_j)\frac{1}{\sqrt{2!}}\big\{|\phi_j(1)\rangle|\phi_j(2)\rangle + |\phi_j(2)\rangle|\phi_j(1)\rangle\big\}, \end{aligned} \tag{3.24}$$

where the coefficient $C(n_j)$ is introduced to assure the normalization condition ${}^+\langle\Psi_{j,j}|\Psi_{j,j}\rangle^+ = 1$. Since the two terms in (3.24) are identical the normalization gives $1 = 4|C(n_j)|^2/2$, i.e. we obtain $C(n_j = 2) = 1/\sqrt{2}$. Repeating this analysis for a state with an arbitrary occupation number n_j, there will be $n_j!$ identical terms, and we obtain the general result $C(n_j) = 1/\sqrt{n_j}$. Finally, if there are several states with occupation numbers $n_1, n_2, \dots$ with $\sum_{p=1}^{\infty} n_p = N$, the normalization constant becomes $C(n_1, n_2, ...) = (n_1!\, n_2! \dots)^{-1/2}$. Thus, for the case of bosons action of the symmetrization operator $\Lambda^+_{1\dots N}$, Eq. (3.14), on the state $|\Psi_{j_1,j_2,\dots j_N}\rangle$ will not yield a normalized state. A normalized symmetric state is obtained by the following prescription,

$$\boxed{|\Psi_{j_1,j_2,\dots j_N}\rangle^+ = \frac{1}{\sqrt{n_1!n_2!\dots}}\,\Lambda^+_{1\dots N}\,|\Psi_{j_1,j_2,\dots j_N}\rangle} \tag{3.25}$$

$$\Lambda^+_{1\dots N} = \frac{1}{\sqrt{N!}}\sum_{P \epsilon S_N} \hat{P}. \tag{3.26}$$

Hence the total prefactor of the symmetric state (the permanent) is $(N!n_1!n_2!...)^{-1/2}$.

An example of the wave function of N bosons is

$$|\Psi_{j_1,j_2,\dots j_N}\rangle^+ = |n_1 n_2 \dots n_k, 0, 0, \dots\rangle, \qquad \sum_{p=1}^{k} n_p = N, \tag{3.27}$$

where $n_p \neq 0$, for all $p \leq k$, whereas all orbitals with the number $p > k$ are empty. In particular, the energetically lowest state of N non-interacting bosons (ground state) is the state where all particles occupy the lowest orbital $|\phi_1\rangle$, i.e. $|\Psi_{j_1,j_2,\dots j_N}\rangle^+_{\text{GS}} = |N0\dots0\rangle$. This effect of a macroscopic population which is possible only for particles with Bose statistics is called *Bose-Einstein condensation.* Note, however, that in the case of interaction between the particles, a permanent constructed from the free single-particle orbitals will not be an eigenstate of the system. In that case, in a Bose condensate a finite fraction of particles will occupy excited orbitals ("condensate depletion"). The construction of the N-particle state for interacting bosons and fermions is subject of the next section.

3.2.5 Interacting bosons and fermions

So far we have assumed that there is no interaction between the particles, and the total hamiltonian is a sum of single-particle hamiltonians. In contrast, in the case of interactions,

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_i + \hat{H}_{\text{int}}, \tag{3.28}$$

and the N-particle wave function will (prior to anti-symmetrization), in general, deviate from a product of single-particle orbitals. Moreover, there is no reason why interacting particles should occupy the single-particle orbitals $|\phi_p\rangle$ of a non-interacting system.

The solution to this problem is based on the fact that the (anti-)symmetric states, $|\Psi_{\{j\}}\rangle^{\pm} = |\{n\}\rangle$, form a complete orthonormal set in the N-particle Hilbert space, cf. Eq. (3.16). This means, any symmetric or antisymmetric state can be represented as a superposition of N-particle permanents or determinants, respectively,

$$\boxed{|\Psi_{\{j\}}\rangle^{\pm} = \sum_{\{n\},\, N=\text{const}} C^{\pm}_{\{n\}} |\{n\}\rangle} \tag{3.29}$$

where the orbitals correspond to the non-interacting problem. The effect of the interaction between the particles on the ground state wave function is to "add" contributions from determinants (permanents) involving higher lying orbitals to the ideal wave function, i.e. the interacting ground state includes contributions from (non-interacting) excited states. For weak interaction, we may expect that energetically low-lying orbitals will give the dominating contribution to the wave function. For example, for two fermions, the dominating states in the expansion (3.29) will be $|1,1,0,\dots\rangle$, $|1,0,1,\dots\rangle$, $|1,0,0,1\dots\rangle$,

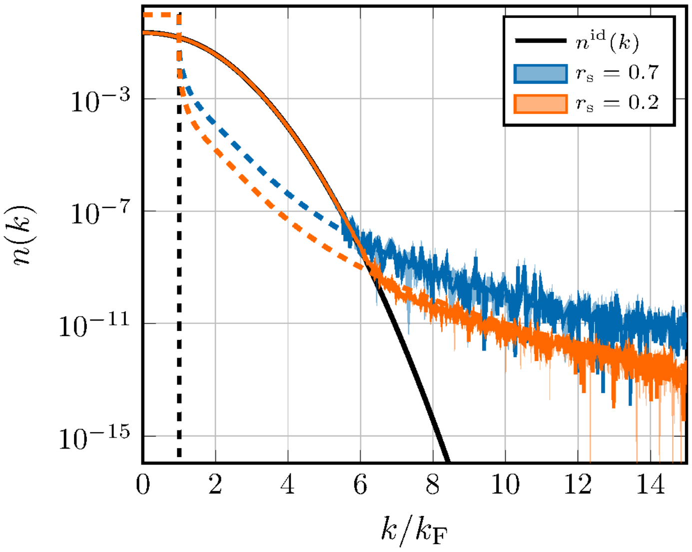

Abbildung 3.2: Momentum distribution function (MDF) of the uniform electron gas at temperature $k_B T = 2E_F$, for two coupling parameters, $r_s = 0.2, 0.7$. The results are obtained from exact CPIMC simulations and compared to the ideal Fermi gas at $T = 0$ (black dashed step function) and the ideal Fermi gas at the same temperature (full line). Note the algebraic decay of the MDF, for large k: $n(k) \sim k^{-8}$, in contrast to the exponential decay of the ideal Fermi function. From Ref. [HSD+21].

$|0, 1, 1, , 0 \dots\rangle$ and so on. The computation of the ground state of an interacting many-particle system is thus transformed into the computation of the expansion coefficients $C^{\pm}_{\{n\}}$. This is the basis of the *exact diagonalization* method or *configuration interaction* (CI). It is obvious that, if we would have obtained the eigenfunctions of the interacting hamiltonian, it would be represented by a diagonal matrix in this basis with the eigenvalues populating the diagonal.[7]

Example: Uniform electron gas ("jellium"). Consider a system of N electrons in a cube of side length L, at a fixed temperature T and a density $n = N/L^3$. The single-particle orbitals are plane waves (eigenfunctions of the momentum operator), $\phi_i(r) = L^{-3/2} e^{i\mathbf{k}_i\mathbf{r}}$, with discrete values of the wave number, k_i, that assure the proper boundary conditions at the box edge. To each wave number corresponds the single-particle energy $\epsilon_i = (\hbar k_i)^2/2m$.

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[7] This N-particle state can be constructed from interacting single-particle orbitals as well. These are called "natural orbitals" and are the eigenvalues of the reduced one-particle density matrix. For a discussion see [SvL13].

1. In the ground state, $T = 0$, particles occupy the N energetically lowest orbitals where particle N occupies the orbital with $k_i = k_F \sim n^{1/3}$, corresponding to the Fermi energy $\epsilon(k_F) = E_F$. The N-particle wave function is then a Slater determinant of these N plane waves. In occupation number representation this wave function has $n_i = 1$, for all $k_i \leq k_F$, and zeroes, for all $k_i > k_F$.

2. At finite temperature, some particles are excited into states above the Fermi energy. This means, the occupation of states around the Fermi edge fluctuates and the mean value is a real number between 0 and 1. This N-particle state cannot be represented by a single Slater determinant of orbitals that are fully occupied ($n_p = 1$) but, instead, it is represented by a weighted average of the ground state and excited states where the weight is given by the Boltzmann factor, $P_k = e^{-E_k/k_B T}$, where $E_k = \sum_{i=1}^{\infty} \epsilon_i n_i^{(k)}$ is the total energy of all particles in the given determinant "k".

3. Finally, in the case of an interacting electron gas, even at $T = 0$, a single determinant is again not sufficient because interactions lead to excitations of particles into orbitals above the Fermi energy. This again gives rise to fractional occupations of the orbitals which corresponds to a superposition of Slater determinants, cf. Eq. (3.29).

This behavior is illustrated in Fig. 3.2. The ideal ground state is shown by the dashed step function whereas the case of finite temperature is depicted by the full line which is nothing but the Fermi distribution that decays exponentially, for large k. The correlated distributions are shown by the orange and blue dashed lines corresponding to weak and moderate Coulomb interaction, respectively. Note that correlation effects lead to a qualitative change of the large k-asymptotic: it is no longer exponential but proportional to k^{-8}. The present results are quasi-exact and do not involve any approximation. They are obtained from Configuration Path Integral Monte Carlo (CPIMC) simulations [SBF$^+$11, HSD$^+$21]. Note the exceptional accuracy of the data which span ten orders of magnitude in the occupation numbers $n(k)$. For an overview on the properties of the interacting electron gas at finite temperature, see Ref. [DGB18].

Configuration Interaction. The approach of computing the N-particle state via a superposition of permanents or determinants can be extended beyond the ground state properties. Indeed, extensions to thermodynamic equilibrium (mixed ensemble where the superpositions carry weights proportional to Boltzmann factors, e.g. [SBF$^+$11]) and also nonequilibrium versions of CI (time-dependent CI, TDCI) that use pure states are meanwhile well established. In the latter, the coefficients become time-dependent, $C^{\pm}_{\{n\}}(t)$, whereas the orbitals remain fixed. We will consider the extension of the occupation number formalism to the thermodynamic properties of interacting bosons and fermions in Chapter 4. Further, nonequilibrium many-particle systems will be considered in Chapters 6 and 8 where we will develop alternative approaches based on reduced density operators and nonequilibrium Green functions, respectively.

The main problem of CI-type methods is the exponential scaling with the system size which we illustrate for a simple example. Consider a system of $N_\uparrow = N_\downarrow = N/2$ electrons and a single-particle basis of $2N_b$ orbitals. Then the total number of determinants $N_{\rm FCI}$ corresponds to the total number of ways $N_\uparrow$ electrons can be placed on N_b orbitals, times the same number for the $N_\downarrow$ electrons:

$$N_{\rm FCI} = \binom{N_b}{N_\uparrow}\binom{N_b}{N_\downarrow} = \left[\frac{N_b!}{(N_\uparrow)!(N_b - N_\uparrow)!}\right]^2 \tag{3.30}$$

For the example of a moderate electron number $N = 10$ and a basis dimension $M = 100$ we obtain $N_{\rm FCI} \sim (100^5/120)^2 \sim 10^{16}$. This “exponential wall” dramatically limits the range of exact quantum mechanical simulations of many-particle systems. This estimate was just for a ground state calculation. For finite temperature the number of required orbitals N_b needed to cover the excitations in the system increases with temperature. In similar manner, in nonequilibrium situations where particles are excited to high energy orbitals N_b may again increase significantly.

Multiconfiguration and restricted active space approaches. To mitigate the exponential efficiency loss of full CI, in recent years a large variety of approximate methods has been developed. Here we mention multiconfiguration (MC) approaches such as MC Hartree or MC Hartree-Fock which exist also in time-dependent variants (MCTDH and MCTDHF), e.g. [MMC90] and are now frequently applied to interacting Bose and Fermi systems. In this method not only the coefficients $C^{\pm}(t)$ are optimized but also the orbitals are adapted in a time-dependent fashion. The main advantage is the reduction of the basis size, as compared to CI. A recent time-dependent application to the photoionization of helium can be found in Ref. [HB11]. Another very general approach consists in subdividing the N-particle state in various classes with different properties. This has been termed “Generalized Active Space” (or restricted active space) approach and is very promising due to its generality [HB12, HB13]. An overview on first results is given in Ref. [HHB14]. Similar approaches have been developed in many other groups, including L. Madsen and co-workers, e.g. [BSM14a] and T. Sato and co-workers [SI13]. An example of application of these methods is presented in Fig. 3.5.

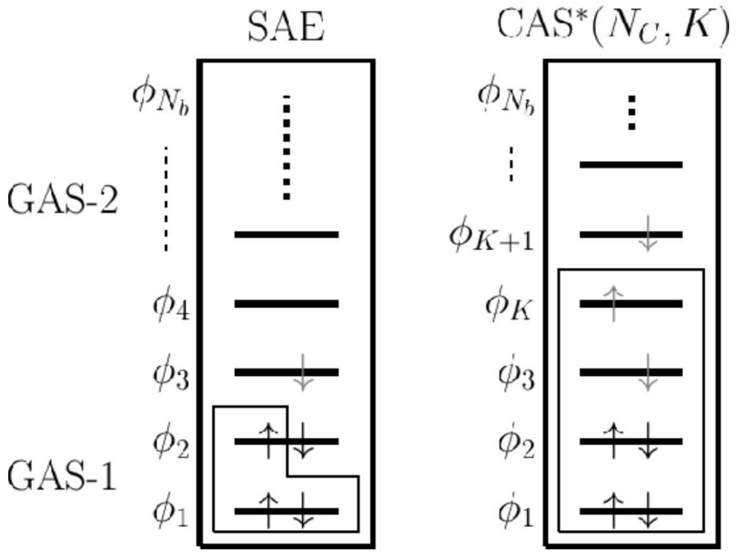

Abbildung 3.3: Illustration of the concept of different "Generalized active spaces" (GAS) for $N = 4$ electrons. Left: single active electron approximation (SAE): 3 electrons are "frozen" in GAS-1, 1 electron is considered "active"; CAS (complete active space): $N_C = 4$ electrons occupy $K \ll N_B$ orbitals in any configuration, for $i > K$ only 1 electron is allowed. The scheme can be easily extended to more general situations.

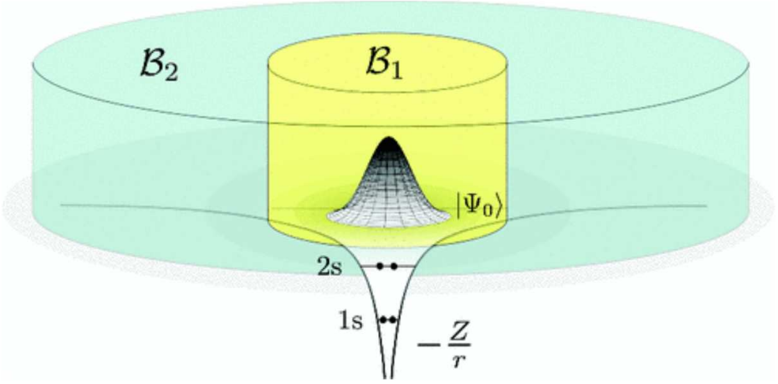

Abbildung 3.4: Hartree-Fock basis (B1) for bound electrons, combined with grid (FE-DVR) basis for continuum states to resolve ionization (B2), from Ref. [HB12].

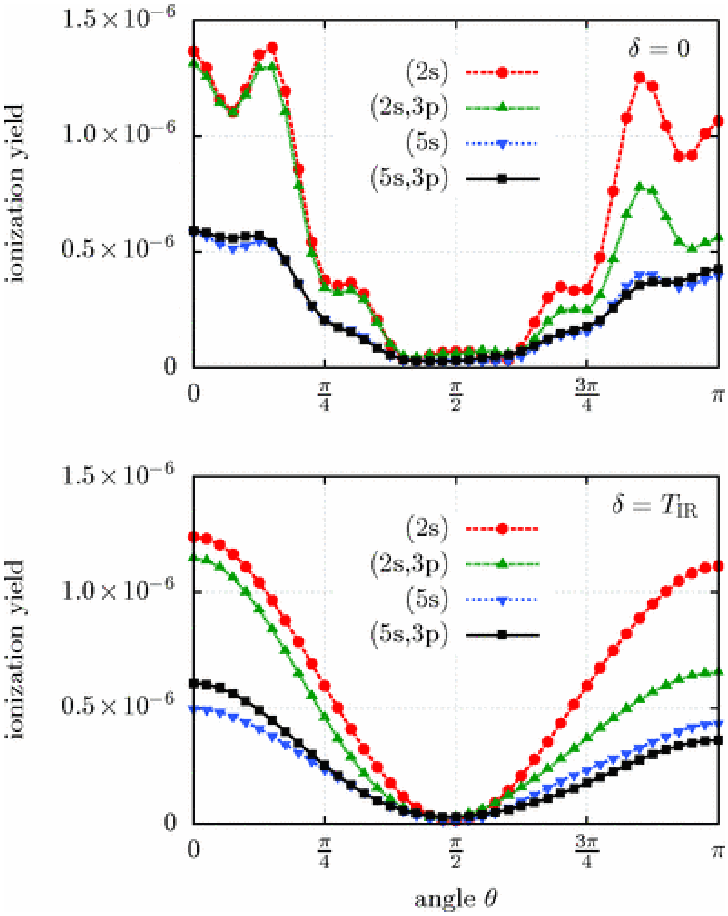

Abbildung 3.5: Angle-resolved photoionization yield (norm of electron wave function outside $r_c = 20a_B$) of beryllium ($N = 4$) for a IR-pump-XUV-probe field and delay δ. 20 cycles XUV-pulse: 200 eV, $10^{12}\mathrm{Wcm}^{-2}$; single-cycle IR-pulse, 780 nm, $10^{11}\mathrm{Wcm}^{-2}$. Comparison of different approximations that take into account a different number of participating orbitals. (2s): TDCIS; (ns,mp): CISD with double excitations up to orbitals ns and mp. From Ref. [HB12].