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 $N = 0, 1, 2, \ldots$,

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

Here, we included the *vacuum state* $|0\rangle = |0, 0, \ldots\rangle$ 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

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

[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 $\Lambda^-_{1\ldots N}$ given by Eq. (3.14). For two particles, we obtain

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

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*,

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

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, $j_1 = 1, j_2 = 2, \ldots j_N = N$, and the state has the simple notation $|1,1,\ldots 1,0,0\ldots\rangle$ 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:

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

3.2.4 Non-interacting many-boson wave function

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

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

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

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

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

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

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 $n_1, n_2, \ldots$ with $\sum_{p=1}^{\infty} n_p = N$, the normalization constant becomes $C(n_1, n_2, ...) = (n_1!\, n_2! \ldots)^{-1/2}$. Thus, for the case of bosons action of the symmetrization operator $\Lambda^+_{1\ldots N}$, Eq. (3.14), on the state $|\Psi_{j_1,j_2,\ldots j_N}\rangle$ will not yield a normalized state. A normalized symmetric state is obtained by the following prescription,

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

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

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

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

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. $|\Psi_{j_1,j_2,\ldots j_N}\rangle^+_{\rm GS} = |N0\ldots0\rangle$. 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,

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

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 dominant contribution to the wave function. For example, for two fermions, the dominating states in the expansion (3.29) will be $|1,1,0,\ldots\rangle$, $|1,0,1,\ldots\rangle$, $|1,0,0,1\ldots\rangle$,

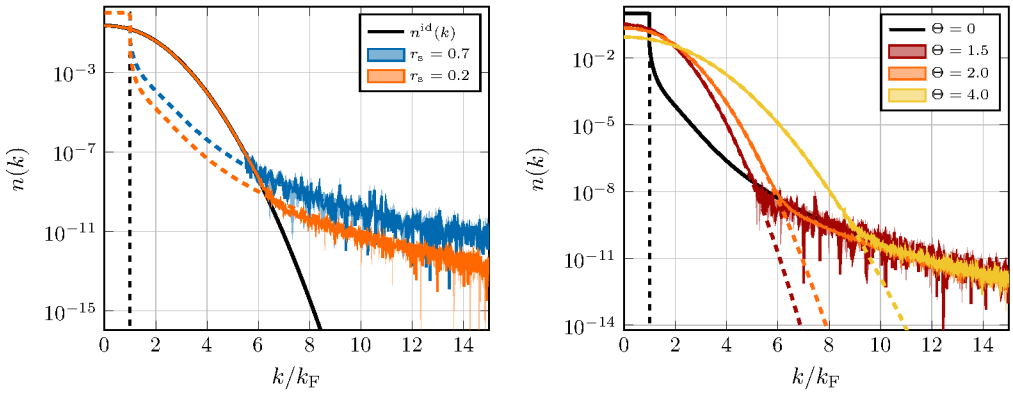

Abbildung 3.2: Momentum distribution function (MDF) of the uniform electron gas. **Left:** at temperature $k_BT = 2E_F$, for two coupling parameters, $r_s = 0.2, 0.7$, **right:** at $r_s = 0.5$ and four temperatures. The results are obtained from exact CPIMC simulations and compared to the ideal Fermi gas at $T = 0$ (black dashed step function) and the ideal Fermi gas at the same temperature (full lines). 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].

$|0, 1, 1, , 0 \ldots\rangle$ 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 $\epsilon_i = (\hbar k_i)^2/2m$.

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

[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].

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, $P_k = e^{-E_k/k_BT}$, 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_{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:

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

For the example of a moderate electron number $N = 10$ and a basis dimension $M = 100$ we obtain $N_{\mathrm{FCI}} \sim (100^5/120)^2 \sim 10^{16}$. 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.

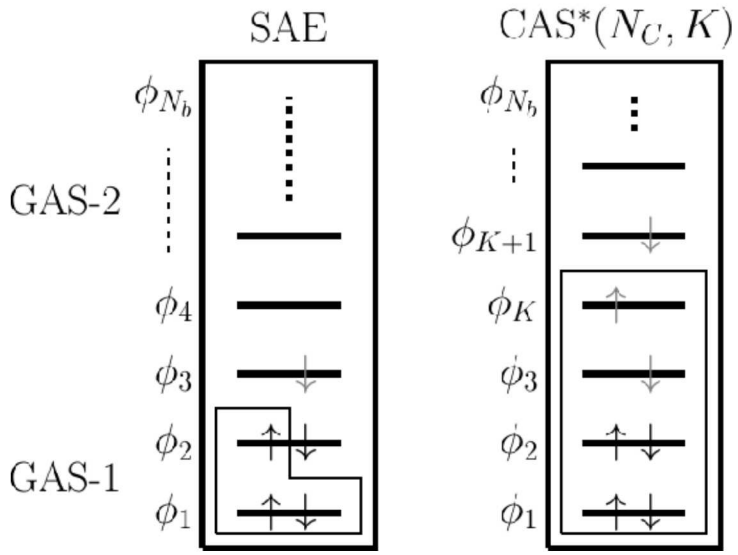

Abbildung 3.3: Illustration of the concept of different "Generalized active spaces" (GAS) for $N = 4$ electrons. Left: single active electron approximation (SAE): 3 electrons are "frozen" in GAS-1, 1 electron is considered "active"; CAS (complete active space): $N_C = 4$ electrons occupy $K \ll N_B$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

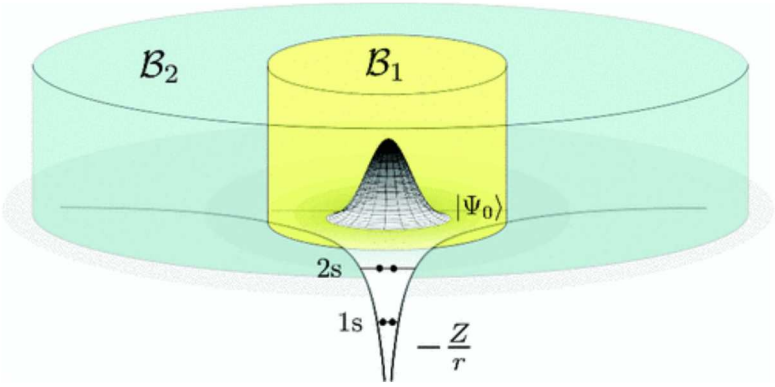

Abbildung 3.4: Hartree-Fock basis (B1) for bound electrons, combined with grid (FE-DVR) basis for continuum states to resolve ionization (B2), from Ref. [HB12].

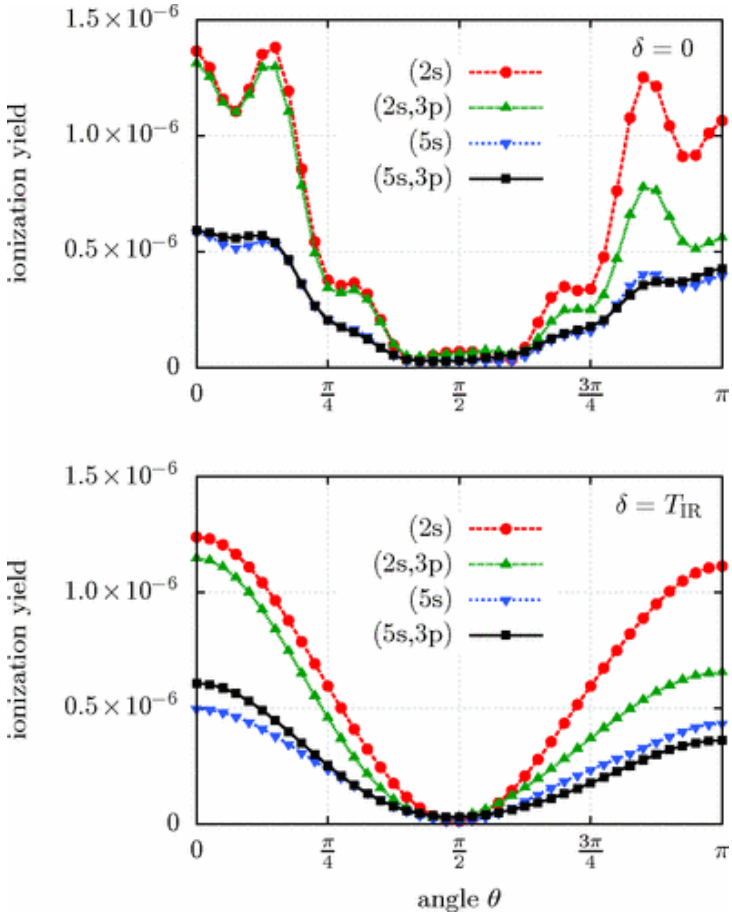

Abbildung 3.5: Angle-resolved photoionization yield (norm of electron wave function outside $r_c = 20a_B$) of beryllium ($N = 4$) for a IR-pump-XUV-probe field and delay δ. 20 cycles XUV-pulse: 200 eV, $10^{12}\mathrm{Wcm}^{-2}$; single-cycle IR-pulse, 780 nm, $10^{11}\mathrm{Wcm}^{-2}$. Comparison of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

3.3 Second quantization for bosons

We have seen in Chapter 1 for the example of the harmonic oscillator that an elegant approach to quantum many-particle systems is given by the method of second quantization. Using properly defined creation and annihilation operators, the hamiltonian of various N-particle systems was diagonalized. The examples studied in Chapter 1 did not explicitly include an interaction contribution to the hamiltonian – a simplification which will now be dropped. We will now consider the full hamiltonian (3.28) and transform it into second quantization representation. While this hamiltonian will, in general, not be diagonal, nevertheless the use of creation and annihilation operators yields a quite efficient approach to the many-particle problem.

3.3.1 Creation and annihilation operators for bosons

We now introduce the creation operator $\hat{a}_i^\dagger$ acting on states from the symmetric Fock space $\mathcal{F}^+$, cf. Sec. 3.2.2. It has the property to increase the occupation number n_i of single-particle orbital $|\phi_i\rangle$ by one. In analogy to the harmonic oscillator, Sec. 2.3 we use the following definition

$$\boxed{\hat{a}_i^\dagger |n_1 n_2 \dots n_i \dots\rangle = \sqrt{n_i+1}\,|n_1 n_2 \dots n_i+1 \dots\rangle} \tag{3.31}$$

While in case of coupled harmonic oscillators this operator created an additional excitation in oscillator "i", now its action leads to a state with an additional particle in orbital "i". The associated annihilation operator $\hat{a}_i$ of orbital $|\phi_i\rangle$ is now constructed as the hermitean adjoint (we use this as its definition) of $\hat{a}_i^\dagger$, i.e. $[\hat{a}_i^\dagger]^\dagger = \hat{a}_i$, and its action can be deduced from the definition (3.31),

$$\begin{aligned}
\hat{a}_i |n_1 n_2 \dots n_i \dots\rangle &= \sum_{\{n'\}} |\{n'\}\rangle\langle\{n'\}|\hat{a}_i|n_1 n_2 \dots n_i \dots\rangle \\
&= \sum_{\{n'\}} |\{n'\}\rangle\langle n_1 n_2 \dots n_i \dots |\hat{a}_i^\dagger|n_1' \dots n_i' \dots\rangle^* = \\
&= \sum_{\{n'\}} \sqrt{n_i'+1}\,\delta^i_{\{n\},\{n'\}}\delta_{n_i,n_i'+1}|\{n'\}\rangle = \\
&= \sqrt{n_i}\,|n_1 n_2 \dots n_i - 1 \dots\rangle,
\end{aligned} \tag{3.32}$$

yielding the same explicit definition that is familiar from the harmonic oscillator[8]: the adjoint of $\hat{a}_i^\dagger$ is indeed an annihilation operator reducing the occupation of orbital $|\phi_i\rangle$ by one. In the third line of Eq. (3.32) we introduced

[8] See our results for coupled harmonic oscillators in section 2.3.2.

the modified Kronecker symbol in which the occupation number of orbital i is missing,

$$\delta^i_{\{n\},\{n'\}} = \delta_{n_1,n'_1}\ldots\delta_{n_{i-1},n'_{i-1}}\delta_{n_{i+1},n'_{i+1}}\ldots. \tag{3.33}$$

$$\delta^{ik}_{\{n\},\{n'\}} = \delta_{n_1,n'_1}\ldots\delta_{n_{i-1},n'_{i-1}}\delta_{n_{i+1},n'_{i+1}}\ldots\delta_{n_{k-1},n'_{k-1}}\delta_{n_{k+1},n'_{k+1}}\ldots. \tag{3.34}$$

In the second line, this definition is extended to two missing orbitals.

We now need to verify the proper bosonic commutation relations, which are given by the

Theorem: The creation and annihilation operators defined by Eqs. (3.31, 3.32) obey the relations

$$[\hat{a}_i,\hat{a}_k] = [\hat{a}^\dagger_i,\hat{a}^\dagger_k] = 0, \qquad \forall i,k, \tag{3.35}$$

$$\left[\hat{a}_i,\hat{a}^\dagger_k\right] = \delta_{i,k}. \tag{3.36}$$

Proof of relation (3.36):
Consider first the case $i \neq k$ and evaluate the commutator acting on an arbitrary state

$$\begin{aligned}\left[\hat{a}_i,\hat{a}^\dagger_k\right]|\{n\}\rangle &= \hat{a}_i\sqrt{n_k+1}|\ldots n_i,\ldots n_k+1\ldots\rangle \\ &\quad -\hat{a}^\dagger_k\sqrt{n_i}|\ldots n_i-1,\ldots n_k\ldots\rangle = 0\end{aligned}$$

Consider now the case $i = k$: Then

$$\left[\hat{a}_k,\hat{a}^\dagger_k\right]|\{n\}\rangle = (n_k+1)|\{n\}\rangle - n_k|\{n\}\rangle = |\{n\}\rangle,$$

which proves the statement since no restrictions with respect to i and k were made. Analogously one proves the relations (3.35), see problem 1[9].

Construction of the N-particle state

As for the harmonic oscillator or any quantized field, an arbitrary many-particle state can be constructed from the vacuum state by repeatedly applying the creation operator(s). For example, single and two-particle states with the proper normalization are obtained via

$$\begin{aligned}|1\rangle &= \hat{a}^\dagger|0\rangle, \\ |0,0\ldots1,0,\ldots\rangle &= \hat{a}^\dagger_i|0\rangle, \\ |0,0\ldots2,0,\ldots\rangle &= \frac{1}{\sqrt{2!}}\left(\hat{a}^\dagger_i\right)^2|0\rangle, \\ |0,0\ldots1,0,\ldots1,0,\ldots\rangle &= \hat{a}^\dagger_i\hat{a}^\dagger_j|0\rangle, \quad i\neq j,\end{aligned}$$

[9]From this property we may also conclude that the ladder operators of the harmonic oscillator have bosonic nature, i.e. the elementary excitations of the oscillator (oscillation quanta or *phonons*) are bosons.

where, in the second (third) line, the 1 (2) stands on position i, whereas in the last line the 1's are at positions i and j. This is readily generalized to an arbitrary symmetric N-particle state according to[10].

$$\boxed{|n_1, n_2, \ldots\rangle = \frac{1}{\sqrt{n_1! n_2! \ldots}} \left(\hat{a}_1^\dagger\right)^{n_1} \left(\hat{a}_2^\dagger\right)^{n_2} \ldots |0\rangle} \tag{3.37}$$

Particle number operators

The operator

$$\boxed{\hat{n}_i = \hat{a}_i^\dagger \hat{a}_i} \tag{3.38}$$

is the *occupation number operator* for orbital i because, for $n_i \geq 1$,

$$\hat{a}_i^\dagger \hat{a}_i |\{n\}\rangle = \hat{a}_i^\dagger \sqrt{n_i} |n_1 \ldots n_i - 1 \ldots\rangle = n_i |\{n\}\rangle,$$

whereas, for $n_i = 0$, $\hat{a}_i^\dagger \hat{a}_i |\{n\}\rangle = 0$. Thus, the symmetric state $|\{n\}\rangle$ is an eigenstate of $\hat{n}_i$ with the eigenvalue coinciding with the occupation number n_i of this state. In other words: all $\hat{n}_i$ have common eigenfunctions with the hamiltonian and commute with it, $[\hat{n}_i, H] = 0$.

The *total particle number operator* is defined as

$$\hat{N} = \sum_{i=1}^{\infty} \hat{n}_i = \sum_{i=1}^{\infty} \hat{a}_i^\dagger \hat{a}_i, \tag{3.39}$$

because its action yields the total number of particles in the system: $\hat{N}|\{n\}\rangle = \sum_{i=1}^{\infty} n_i |\{n\}\rangle = N|\{n\}\rangle$. Thus, also $\hat{N}$ commutes with the hamiltonian and has the same eigenfunctions.

Single-particle operators

Consider now a general single-particle operator[11] defined as

$$\hat{B}_1 = \sum_{\alpha=1}^{N} \hat{b}_\alpha, \tag{3.40}$$

where $\hat{b}_\alpha$ acts only on the variables associated with particle with number "α". We will now transform this operator into second quantization representation.

[10] The origin of the prefactors was discussed in Sec. 3.2.4 and is also analogous to the case of the harmonic oscillator Sec. 2.3.

[11] Examples are the total momentum, total kinetic energy, angular momentum or potential energy of the system.

To this end we define the matrix element with respect to the single-particle orbitals

$$b_{ij} = \langle i|\hat{b}|j\rangle, \tag{3.41}$$

and the generalized projection operator[12]

$$\hat{\Pi}_{ij} = \sum_{\alpha=1}^{N} |i\rangle_\alpha \langle j|_\alpha, \tag{3.42}$$

where $|i\rangle_\alpha$ denotes the orbital i occupied by particle α.

Theorem: The second quantization representation of a single-particle operator is given by

$$\boxed{\hat{B}_1 = \sum_{i,j=1}^{\infty} b_{ij}\, \hat{\Pi}_{ij} = \sum_{i,j=1}^{\infty} b_{ij}\, \hat{a}_i^\dagger \hat{a}_j} \tag{3.43}$$

Proof:
We first expand $\hat{b}$, for an arbitrary particle α, into a basis of single-particle orbitals, $|i\rangle = |\phi_i\rangle$,

$$\hat{b} = \sum_{i,j=1}^{\infty} |i\rangle\langle i|\hat{b}|j\rangle\langle j| = \sum_{i,j=1}^{\infty} b_{ij}|i\rangle\langle j|,$$

where we used the definition (3.41) of the matrix element. With this result we can transform the total operator, Eq. (3.40), using the definition (3.42),

$$\hat{B}_1 = \sum_{\alpha=1}^{N}\sum_{i,j=1}^{\infty} b_{ij}|i\rangle_\alpha\langle j|_\alpha = \sum_{i,j=1}^{\infty} b_{ij}\hat{\Pi}_{ij}, \tag{3.44}$$

We now express $\hat{\Pi}_{ij}$ in terms of creation and annihilation operators by analyzing its action on a symmetric state (3.25), taking into account that $\hat{\Pi}_{ij}$ commutes with the symmetrization operator $\Lambda^+_{1\ldots N}$, Eq. (3.26)[13],

$$\hat{\Pi}_{ij}|\{n\}\rangle \;=\; \frac{1}{\sqrt{n_1!n_2!\ldots}}\,\Lambda^+_{1\ldots N}\sum_{\alpha=1}^{N}|i\rangle_\alpha\langle j|_\alpha\;\cdot|j_1\rangle|j_2\rangle\ldots|j_N\rangle. \tag{3.45}$$

[12]For $i = j$ this definition contains the standard projection operator on state $|i\rangle$, i.e. $|i\rangle\langle i|$, whereas for $i \neq j$ this operator projects onto a transition, i.e. transfers an arbitrary particle from state $|j\rangle$ to state $|i\rangle$.

[13]From the definition (3.42) it is obvious that $\hat{\Pi}_{ij}$ is totally symmetric in all particle indices.

The product state is constructed from all orbitals that are occupied by the N particles and, in general, includes the orbitals $|i\rangle$ and $|j\rangle$. In general, these orbitals will be present n_i and n_j times, respectively (there is no Pauli principle). Let us consider two cases.
1) $j \neq i$: Since the single-particle orbitals form an orthonormal basis, $\langle j|j\rangle = 1$, multiplication with $\langle j|_\alpha$ reduces the number of occurences of orbital $|j\rangle$ in the product state by one, whereas multiplication with $|i\rangle_\alpha$ increases the number of orbitals $|i\rangle$ by one. The occurence of n_j such orbitals (occupied by n_j particles) in the product state gives rise to an overall factor of n_j because n_j terms of the sum will yield a non-vanishing contribution.

Finally, we compare this result to the properly symmetrized state which follows from $|\{n\}\rangle$ by increasing n_i by one and decreasing n_j by one, which will be denoted by

$$\begin{aligned} \left|\{n\}_j^i\right\rangle &= |n_1, n_2 \ldots n_i + 1 \ldots n_j - 1 \ldots\rangle \\ &= \frac{1}{\sqrt{n_1! \ldots (n_i+1)! \ldots (n_j-1)! \ldots}} \Lambda^+_{1\ldots N} \cdot |j_1\rangle|j_2\rangle \ldots |j_N\rangle. \end{aligned} \tag{3.46}$$

It contains the same particle number N as the state $|\{n\}\rangle$ but, due to the different orbital occupations, the prefactor in front of $\Lambda^+_{1\ldots N}$ differs by $\sqrt{n_j}/\sqrt{n_i+1}$, compared to the one in Eq. (3.45) which we, therefore, can rewrite as

$$\begin{aligned} \hat{\Pi}_{ij}|\{n\}\rangle &= n_j \frac{\sqrt{n_i+1}}{\sqrt{n_j}} \left|\{n\}_j^i\right\rangle \\ &= \hat{a}_i^\dagger \hat{a}_j |\{n\}\rangle. \end{aligned} \tag{3.47}$$

2), $j = i$: The same derivation now leads again to a number n_j of factors, whereas the square roots in Eq. (3.47) compensate each other, and we obtain

$$\begin{aligned} \hat{\Pi}_{jj}|\{n\}\rangle &= n_j \ |\{n\}\rangle \\ &= \hat{a}_j^\dagger \hat{a}_j |\{n\}\rangle. \end{aligned} \tag{3.48}$$

Thus, the results (3.47) and (3.48) can be combined to the operator identity

$$\boxed{\hat{\Pi}_{ij} = \sum_{\alpha=1}^{N} |i\rangle_\alpha \langle j|_\alpha = \hat{a}_i^\dagger \hat{a}_j} \tag{3.49}$$

which, together with the definition (3.46), proves the theorem[14].

[14] See problem 2.

For the special case that the orbitals are eigenfunctions of an operator, $\hat{b}_\alpha|\phi_i\rangle = b_i|\phi_i\rangle$—such as the single-particle hamiltonian, the corresponding matrix is diagonal, $b_{ij} = b_i\delta_{ij}$, and the representation (3.43) simplifies to

$$\hat{B}_1 = \sum_{i=1}^{\infty} b_i\, \hat{a}_i^\dagger \hat{a}_i = \sum_{i=1}^{\infty} b_i\, \hat{n}_i, \tag{3.50}$$

where b_i are the eigenvalues of $\hat{b}$. Equation (3.50) naturally generalizes the familiar spectral representation of quantum mechanical operators to the case of many-body systems with arbitrary variable particle number.

Two-particle operators

A two-particle operator is of the form

$$\hat{B}_2 = \frac{1}{2!} \sum_{\alpha\neq\beta=1}^{N} \hat{b}_{\alpha,\beta}, \tag{3.51}$$

where $\hat{b}_{\alpha,\beta}$ acts only on particles α and β. An example is the operator of the pair interaction, $\hat{b}_{\alpha,\beta} \to w(|\mathbf{r}_\alpha - \mathbf{r}_\beta|)$. We introduce again matrix elements, now with respect to two-particle states composed as products of single-particle orbitals, which belong to the two-particle Hilbert space $\mathcal{H}_2 = \mathcal{H}_1 \otimes \mathcal{H}_1$,

$$b_{ijkl} = \langle ij|\hat{b}|kl\rangle, \tag{3.52}$$

Theorem: The second quantization representation of a two-particle operator is given by

$$\boxed{\hat{B}_2 = \frac{1}{2!} \sum_{i,j,k,l=1}^{\infty} b_{ijkl}\, \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k} \tag{3.53}$$

Proof:
We expand $\hat{b}$ for an arbitrary pair α, β into a basis of two-particle orbitals $|ij\rangle = |\phi_i\rangle|\phi_j\rangle$,

$$\hat{b} = \sum_{i,j,k,l=1}^{\infty} |ij\rangle\langle ij|\hat{b}|kl\rangle\langle kl| = \sum_{i,j,k,l=1}^{\infty} |ij\rangle\langle kl|\; b_{ijkl},$$

leading to the following result for the total two-particle operator,

$$\hat{B}_2 = \frac{1}{2!} \sum_{i,j,k,l=1}^{\infty} b_{ijkl} \sum_{\alpha\neq\beta=1}^{N} |i\rangle_\alpha |j\rangle_\beta \langle k|_\alpha \langle l|_\beta. \tag{3.54}$$

The second sum is readily transformed, using the property (3.49) of the sigle-particle states. We first extend the summation over the particles to include $\alpha = \beta$,

$$\begin{aligned}\sum_{\alpha\neq\beta=1}^{N} |i\rangle_\alpha|j\rangle_\beta\langle k|_\alpha\langle l|_\beta &= \sum_{\alpha=1}^{N} |i\rangle_\alpha\langle k|_\alpha \sum_{\beta=1}^{N} |j\rangle_\beta\langle l|_\beta - \delta_{k,j}\sum_{\alpha=1}^{N} |i\rangle_\alpha\langle l|_\alpha \\ &= \hat{a}_i^\dagger\hat{a}_k\hat{a}_j^\dagger\hat{a}_l - \delta_{k,j}\,\hat{a}_i^\dagger\hat{a}_l \\ &= \hat{a}_i^\dagger\left\{\hat{a}_j^\dagger\hat{a}_k + \delta_{k,j}\right\}\hat{a}_l - \delta_{k,j}\,\hat{a}_i^\dagger\hat{a}_l \\ &= \hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_k\hat{a}_l.\end{aligned}$$

In the third line we have used the commutation relation (3.36). After exchanging the order of the two annihilators (they commute) and inserting this expression into Eq. (3.54), we obtain the final result (3.53)[15].

General many-particle operators

The above results are directly extended to more general operators involving K particles out of N

$$\boxed{\hat{B}_K = \frac{1}{K!}\sum_{\alpha_1\neq\alpha_2\neq\ldots\alpha_K=1}^{N} \hat{b}_{\alpha_1,\ldots\alpha_K},} \tag{3.55}$$

and which have the second quantization representation

$$\boxed{\hat{B}_K = \frac{1}{K!}\sum_{j_1\ldots j_k m_1\ldots m_k=1}^{\infty} b_{j_1\ldots j_k m_1\ldots m_k}\,\hat{a}_{j_1}^\dagger\ldots\hat{a}_{j_k}^\dagger\hat{a}_{m_k}\ldots.\hat{a}_{m_1}} \tag{3.56}$$

where we used the general matrix elements with respect to k-particle product states, $b_{j_1\ldots j_k m_1\ldots m_k} = \langle j_1\ldots j_k|\hat{b}|m_1\ldots m_k\rangle$. Note again the inverse ordering of the annihilation operators. Obviously, the result (3.56) includes the previous examples of single and two-particle operators as special cases.

Comment: of course, our goal is to compute expectation values of operators that correctly incorporate the spin statistics of the particles. It may look, therefore, counter-intuitive, that the second quantization representation of $\hat{B}_K, K \geq 2$ includes matrix elements with non-(anti-)symmetric K-particle

[15]Note that the order of the creation operators and of the annihilators, respectively, is arbitrary. In Eq. (3.53) we have chosen an ascending order of the creators (same order as the indices of the matrix element) and a descending order of the annihilators, since this leads to an expression which is the same for Bose and Fermi statistics, cf. Sec. 3.4.1.

states (product states). However, this is not a contradiction. The spin statistics are taken care of by the creation and annihilation operates. The matrix elements can be computed with any set of states, as long as they span the relevant K-particle Hilbert space[16].

3.4 Second quantization for fermions

We now turn to particles with half-integer spin, i.e. fermions, which are described by anti-symmetric wave functions and obey the Pauli principle, cf. Sec. 3.2.3.

3.4.1 Creation and annihilation operators for fermions

As for bosons we wish to introduce creation and annihilation operators that should again allow for the construction of any many-body state out of the vacuum state, according to [cf. Eq. (3.37)]

$$|n_1, n_2, \dots\rangle = \Lambda^-_{1\dots N}|i_1 \dots i_N\rangle = \left(\hat{a}_1^\dagger\right)^{n_1}\left(\hat{a}_2^\dagger\right)^{n_2}\dots|0\rangle. \qquad n_i = 0, 1, \quad (3.57)$$

Due to the Pauli principle we expect that there will be no additional prefactors resulting from multiple occupations of orbitals, as in the case of bosons[17]. So far we do not know how these operators look like explicitly. Their definition has to make sure that the N-particle states have the correct anti-symmetry and that application of any creator (or annihilator) more than once will return zero.

Example: $N = 2$. To solve this problem, consider two fermions which can occupy the orbitals k or l. The two-particle state has the symmetry $|kl\rangle = -|lk\rangle$, upon particle exchange. The anti-symmetrized state is constructed of the product state of particle 1 in state k and particle 2 in state l and has the properties

$$\Lambda^-_{1\dots N}|kl\rangle = \hat{a}_l^\dagger\hat{a}_k^\dagger|0\rangle = |11\rangle = -\Lambda^-_{1\dots N}|lk\rangle = -\hat{a}_k^\dagger\hat{a}_l^\dagger|0\rangle, \quad (3.58)$$

i.e., it changes sign upon exchange of the particles (third equality). This indicates that the state depends on the order in which the orbitals are filled, i.e., on the order of action of the two creation operators. One possible choice is

[16] This is the same approach as has been used in the construction of the N-particle wave function of an interacting system in Sec. 3.2.5.

[17] The prefactors are always equal to unity because $1! = 1$.

used in the above equation and immediately implies that[18]

$$\hat{a}_k^\dagger \hat{a}_l^\dagger + \hat{a}_l^\dagger \hat{a}_k^\dagger = [\hat{a}_k^\dagger, \hat{a}_l^\dagger]_+ = 0, \qquad \forall k, l, \tag{3.59}$$

where we have introduced the *anti-commutator*[19]. In the special case, $k = l$, we immediately obtain $\left(\hat{a}_k^\dagger\right)^2 = 0$, for an arbitrary state, in agreement with the Pauli principle. Calculating the hermitean adjoint of Eq. (3.59) we obtain that the anti-commutator of two annihilators vanishes as well,

$$[\hat{a}_k, \hat{a}_l]_+ = 0, \qquad \forall k, l. \tag{3.60}$$

We expect that this property holds for any two orbitals k, l and for any N-particle state that involves these orbitals since our consideration did not depend on a specific case.

Now we can introduce an explicit definition of the fermionic creation operator which has all these properties. The operator creating a fermion in orbital k of a general many-body state is defined as[20]

$$\boxed{\hat{a}_k^\dagger |\dots, n_k, \dots\rangle = (1 - n_k)(-1)^{\alpha_k} |\dots, n_k + 1, \dots\rangle, \quad \alpha_k = \sum_{l<k} n_l} \tag{3.61}$$

where the prefactor explicitly enforces the Pauli principle, and the sign factor takes into account the position of the orbital k in the many-fermion state and the number of fermions standing "to the left" of the "newly created" particle, cf. Fig. 3.6. In other words, with α_k pair exchanges (anti-commutations) the particle would move from the leftmost place to the position (e.g. according to an ordering with respect to the orbital energies E_k) of orbital k in the N-particle state. We now derive the annihilation operator by inserting a complete

[18] We can leave out the state $|0\rangle$ on which the operators act because our derivation can be repeated for any state.

[19] This was introduced by P. Jordan and E. Wigner in 1927. Sometimes the anticommutator is denoted with curly brackets, $\{\hat{A}, \hat{B}\}$.

[20] There can be other conventions which differ from ours by the choice of the exponent α_k which, however, is irrelevant for physical observables.

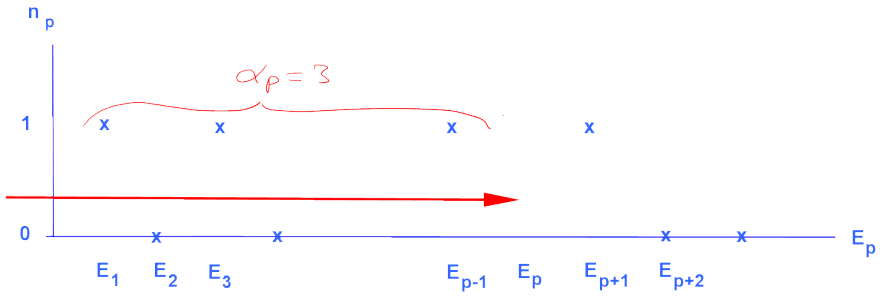

Abbildung 3.6: Illustration of the phase factor α in the fermionic creation and annihilation operators. A fermion is added to orbital "p" (red arrow) and has to be moved past three singly occupied orbitals ($n_p = 1$) with lower energy. This requires $\alpha_p = 3$ pair exchanges, i.e. a sign change will occur. Particles in orbitals with higher energy do not influence the sign. The single-particle orbitals are assumed to be in a definite order (e.g. with respect to the energy eigenvalues).

set of anti-symmetric states and using (3.61)

$$\begin{aligned}
\hat{a}_k|\ldots,n_k,\ldots\rangle &= \sum_{\{n'\}}|\{n'\}\rangle\langle\{n'\}|\hat{a}_k|\ldots,n_k,\ldots\rangle = \\
&= \sum_{\{n'\}}|\{n'\}\rangle\langle\{n\}|\hat{a}_k^\dagger|\{n'\}\rangle^* \\
&= \sum_{\{n'\}}(1-n'_k)(-1)^{\alpha'_k}\delta^k_{\{n'\},\{n\}}\delta_{n_k,n'_k+1}|\{n'\}\rangle \\
&= (2-n_k)(-1)^{\alpha_k}|\ldots,n_k-1,\ldots\rangle \\
&\equiv n_k(-1)^{\alpha_k}|\ldots,n_k-1,\ldots\rangle
\end{aligned}$$

where, in the third line, we used definition (3.33). Also, $\alpha'_k = \alpha_k$ because the sum involves only occupation numbers that are not altered. Note that the factor $2 - n_k = 1$, for $n_k = 1$. However, for $n_k = 0$ the present result is not correct, as it should return zero. To this end, in the last line we have added the factor n_k that takes care of this case. At the same time this factor does not alter the result for $n_k = 1$. Thus, the factor $2 - n_k$ can be skipped entirely, and we obtain the expression for the fermionic annihilation operator of a particle

in orbital k

$$\boxed{\hat{a}_k|\ldots,n_k,\ldots\rangle = n_k(-1)^{\alpha_k}|\ldots,n_k-1,\ldots\rangle} \tag{3.62}$$

Using the definitions (3.61) and (3.62) one readily proves the anti-commutation relations given by the

Theorem: The creation and annihilation operators defined by Eqs. (3.61) and (3.62) obey the relations

$$[\hat{a}_i,\hat{a}_k]_+ = [\hat{a}_i^\dagger,\hat{a}_k^\dagger]_+ = 0, \qquad \forall i,k, \tag{3.63}$$

$$\left[\hat{a}_i,\hat{a}_k^\dagger\right]_+ = \delta_{i,k}. \tag{3.64}$$

Proof of relation (3.63):
Consider, the case of two annihilators and the action on an arbitrary anti-symmetric state

$$[\hat{a}_i,\hat{a}_k]_+|\{n\}\rangle = (\hat{a}_i\hat{a}_k + \hat{a}_k\hat{a}_i)\,|\{n\}\rangle, \tag{3.65}$$

and consider first case $i=k$. Inserting the definition (3.62), we obtain

$$(\hat{a}_k)^2\,|\{n\}\rangle \sim n_k\hat{a}_k|n_1\ldots n_k-1\ldots\rangle = 0,$$

and thus the anti-commutator vanishes as well. Consider now the case[21] $i<k$:

$$\begin{aligned}\hat{a}_i\hat{a}_k|\{n\}\rangle &= \hat{a}_i n_k(-1)^{\sum_{l<k}n_l}|n_1\ldots n_k-1\ldots\rangle = \\ &= n_i n_k(-1)^{\sum_{l<k}n_l}(-1)^{\sum_{l<i}n_l}|n_1\ldots n_i-1\ldots n_k-1\ldots\rangle.\end{aligned}$$

Now we compute the result of the action of the exchanged operator pair

$$\begin{aligned}\hat{a}_k\hat{a}_i|\{n\}\rangle &= \hat{a}_k n_i(-1)^{\sum_{l<i}n_l}|n_1\ldots n_i-1\ldots\rangle = \\ &= n_i n_k(-1)^{\sum_{l<i}n_l}(-1)^{\sum_{l<k}n_l-1}|n_1\ldots n_i-1\ldots n_k-1\ldots\rangle,\end{aligned}$$

The only difference compared to the first result is in the additional -1 in the second exponent. It arises because, upon action of $\hat{a}_k$ after $\hat{a}_i$, the number of particles to the left of k is already reduced by one. Thus, the two expressions differ just by a minus sign, which proves vanishing of the anti-commutator.

The proof of relation (3.64) proceeds analogously and is subject of Problem 3, cf. Sec. 3.9.

Thus we have proved all anti-commutation relations for the fermionic operators and confirmed that the definitions (3.61) and (3.62) obey all properties required for fermionic field operators. We can now proceed to use these operators to bring arbitrary quantum-mechanical operators into second quantized form in terms of fermionic orbitals.

[21] This covers the general case of $i \neq k$, since i and k are arbitrary.

Particle number operators

As in the case of bosons, the operator

$$\boxed{\hat{n}_i = \hat{a}_i^\dagger \hat{a}_i} \tag{3.66}$$

is the *occupation number operator* for orbital i because, for $n_i = 0, 1$,

$$\hat{a}_i^\dagger \hat{a}_i |\{n\}\rangle = \hat{a}_i^\dagger (-1)^{\alpha_i} n_i |n_1 \dots n_i - 1 \dots\rangle = n_i[1 - (n_i - 1)]|\{n\}\rangle,$$

where the prefactor equals n_i, for $n_i = 1$ and zero otherwise. Thus, the anti-symmetric state $|\{n\}\rangle$ is an eigenstate of $\hat{n}_i$ with the eigenvalue coinciding with the occupation number n_i of this state[22].
The *total particle number operator* is defined as

$$\hat{N} = \sum_{i=1}^{\infty} \hat{n}_i = \sum_{i=1}^{\infty} \hat{a}_i^\dagger \hat{a}_i, \tag{3.67}$$

because its action yields the total particle number:
$\hat{N}|\{n\}\rangle = \sum_{i=1}^{\infty} n_i |\{n\}\rangle = N|\{n\}\rangle$.

Single-particle operators

Consider now again a single-particle operator

$$\hat{B}_1 = \sum_{\alpha=1}^{N} \hat{b}_\alpha, \tag{3.68}$$

and let us find its second quantization representation.
Theorem: The second quantization representation of a single-particle operator is given by

$$\boxed{\hat{B}_1 = \sum_{i,j=1}^{\infty} b_{ij}\, \hat{a}_i^\dagger \hat{a}_j} \tag{3.69}$$

Proof:
As for bosons, cf. Eq. (3.44), we have

$$\hat{B}_1 = \sum_{\alpha=1}^{N} \sum_{i,j=1}^{\infty} b_{ij} |i\rangle_\alpha \langle j|_\alpha = \sum_{i,j=1}^{\infty} b_{ij} \hat{\Pi}_{ij}, \tag{3.70}$$

[22]This result, together with the anti-commutation relations for the operators a and $a^\dagger$ proves the consistency of the definitions (3.61) and (3.62).

where $\hat{\Pi}_{ij}$ was defined by (3.42), and it remains to show that $\hat{\Pi}_{ij} = \hat{a}_i^\dagger \hat{a}_j$, for fermions as well. To this end we consider action of $\hat{\Pi}_{ij}$ on an anti-symmetric state, taking into accont that $\hat{\Pi}_{ij}$ commutes with the anti-symmetrization operator $\Lambda^-_{1\ldots N}$, Eq. (3.14),

$$\hat{\Pi}_{ij}|\{n\}\rangle = \frac{1}{\sqrt{N!}} \sum_{\alpha=1}^{N} \sum_{\pi \epsilon S_N} \mathrm{sign}(\pi) |i\rangle_\alpha \langle j|_\alpha \cdot |j_1\rangle_{\pi(1)} |j_2\rangle_{\pi(2)} \ldots |j_N\rangle_{\pi(N)}. \quad (3.71)$$

If the product state does not contain the orbital $|j\rangle$ expression (3.71) vanishes, due to the orthogonality of the orbitals. Otherwise, let $j_k = j$. Then $\langle j|j_k\rangle = 1$, and the orbital $|j_k\rangle$ will be replaced by $|i\rangle$, unless the state $|i\rangle$ is already present, then we again obtain zero due to the Pauli principle, i.e.

$$\hat{\Pi}_{ij}|\{n\}\rangle \quad \sim \quad (1-n_i) n_j \left|\{n\}_j^i\right\rangle, \quad (3.72)$$

where we used the notation (3.46). What remains is to figure out the sign change due to the removal of a particle from the j-th orbital and creation of one in the i-th orbital. To this end we first "move" the (empty) orbital $|j\rangle$ past all orbitals to the left that are occupied by $\alpha_j = \sum_{p<j} n_p$ particles, requiring just α_j pair permutations and sign changes. Next we move the "new" particle to orbital "i" past $\alpha_i = \sum_{p<i} n_p$ particles occupying the orbitals with an energy lower then E_i leading to α_i pair exchanges and sign changes[23]. Taking into account the definitions (3.61) and (3.62) we obtain[24]

$$\boxed{\hat{\Pi}_{ij}|\{n\}\rangle = (-1)^{\alpha_i+\alpha_j}(1-n_i)n_j \left|\{n\}_j^i\right\rangle = \hat{a}_i^\dagger \hat{a}_j |\{n\}\rangle} \quad (3.73)$$

which, together with the equation (3.70), proves the theorem. Thus, the second quantization representation of single-particle operators is the same for bosons and fermions.

Two-particle operators

As for bosons, we now derive the second quantization representation of a two-particle operator $\hat{B}_2$.

[23]Note that, if $i > j$, the occupation numbers occuring in α_i have changed by one compared to those in α_j.

[24]One readily verifies that this result applies also to the case $j = i$. Then the prefactor is just $[1-(n_j-1)]n_j = n_j$, and $\alpha_i = \alpha_j$, resulting in a plus sign

$$\hat{\Pi}_{jj}|\{n\}\rangle \quad = \quad n_j \ |\{n\}\rangle = \hat{a}_j^\dagger \hat{a}_j |\{n\}\rangle.$$

Theorem: The second quantization representation of a two-particle operator is given by

$$\boxed{\hat{B}_2 = \frac{1}{2!} \sum_{i,j,k,l=1}^{\infty} b_{ijkl}\, \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k} \tag{3.74}$$

Proof:
As for bosons, we expand $\hat{B}$ into a basis of two-particle orbitals $|ij\rangle = |\phi_i\rangle|\phi_j\rangle$,

$$\hat{B}_2 = \frac{1}{2!} \sum_{i,j,k,l=1}^{\infty} b_{ijkl} \sum_{\alpha\neq\beta=1}^{N} |i\rangle_\alpha |j\rangle_\beta \langle k|_\alpha \langle l|_\beta, \tag{3.75}$$

and transform the second sum

$$\begin{aligned}
\sum_{\alpha\neq\beta=1}^{N} |i\rangle_\alpha |j\rangle_\beta \langle k|_\alpha \langle l|_\beta &= \sum_{\alpha=1}^{N} |i\rangle_\alpha \langle k|_\alpha \sum_{\beta=1}^{N} |j\rangle_\beta \langle l|_\beta - \delta_{k,j} \sum_{\alpha=1}^{N} |i\rangle_\alpha \langle l|_\alpha \\
&= \hat{a}_i^\dagger \hat{a}_k \hat{a}_j^\dagger \hat{a}_l - \delta_{k,j}\, \hat{a}_i^\dagger \hat{a}_l \\
&= \hat{a}_i^\dagger \left\{ -\hat{a}_j^\dagger \hat{a}_k + \delta_{k,j} \right\} \hat{a}_l - \delta_{k,j}\, \hat{a}_i^\dagger \hat{a}_l \\
&= -\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l .
\end{aligned}$$

In the third line we have used the anti-commutation relation (3.64). After exchanging the order of the two annihilators, which now leads to a sign change and, inserting this expression into Eq. (3.75), we obtain the final result (3.74).

Comment: from the derivation it is clear that there exist a variety of equivalent representations of two-particle operators that are obtained by interchanging pairs of field operators. Here we note one that is obtained when we retain the original alternating order of creation and annihilation operators. Introducing the single-particle density operator $\hat{n}_{ij} = \hat{a}_i^\dagger \hat{a}_j$

$$\hat{B}_2 = \frac{1}{2!} \sum_{i,j,k,l=1}^{\infty} b_{ijkl} \left\{ \hat{n}_{ik} \hat{n}_{jl} - \delta_{kj} \hat{n}_{il} \right\} . \tag{3.76}$$

General many-particle operators

The above results are directly extended to a general K-particle operator, $K \leq N$, which was defined in Eq. (3.55). Its second quantization representation is found to be

$$\boxed{\hat{B}_K = \frac{1}{K!} \sum_{j_1 \ldots j_k m_1 \ldots m_k=1}^{\infty} b_{j_1 \ldots j_k m_1 \ldots m_k}\, \hat{a}_{j_1}^\dagger \ldots \hat{a}_{j_k}^\dagger \hat{a}_{m_k} \ldots . \hat{a}_{m_1}} \tag{3.77}$$

where we used the general matrix elements with respect to k-particle product states, $b_{j_1\ldots j_k m_1\ldots m_k} = \langle j_1 \ldots j_k|\hat{b}|m_1 \ldots m_k\rangle$. Note again the inverse ordering of the annihilation operators which exactly agrees with the expression for a bosonic system. Obviously, the result (3.77) includes the previous examples of single and two-particle operators as special cases.

3.5 Coordinate representation of second quantization operators. Field operators

So far we have considered the creation and annihilation operators in an arbitrary basis of single-particle states. The coordinate and momentum representations are of particular importance and will be considered in the following. As before, an advantage of the present second quantization approach is that these considerations are entirely analogous for fermions and bosons and can be performed at once for both, the only differences being the details of the commutation (anticommutation) rules of the respective creation and annihilation operators and the different orbital occupation numbers. Here we start with the coordinate representation, whereas the momentum representation will be introduced below, in Sec. 3.6.

3.5.1 Definition of field operators

We now introduce operators that create or annihilate a particle at a given space point rather than in given orbital $\phi_i(r)$. To this end we consider the superposition in terms of the functions $\phi_i(r)$ where the coefficients are the creation and annihilation operators,

$$\hat{\psi}(x) = \sum_{i=1}^{\infty} \phi_i(x)\hat{a}_i, \tag{3.78}$$

$$\hat{\psi}^\dagger(x) = \sum_{i=1}^{\infty} \phi_i^*(x)\hat{a}_i^\dagger. \tag{3.79}$$

Here $x = (\mathbf{r}, \sigma)$, i.e. $\phi_i(x)$ is an eigenstate of the operator $\hat{\mathbf{r}}$, and the $\phi_i(x)$ form a complete orthonormal set. Obviously, these operators have the desired property to create (annihilate) a particle at space point $\mathbf{r}$ in spin state σ. From the (anti-)symmetrization properties of the operators a and $a^\dagger$ we immediately

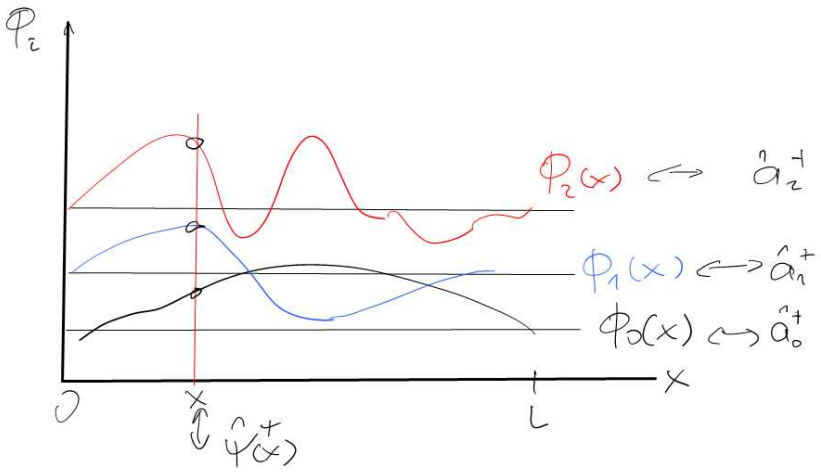

Abbildung 3.7: Illustration of the relation of the field operators to the second quantization operators defined on a general basis $\{\phi_i(x)\}$. The field operator $\hat{\psi}^\dagger(x)$ creates a particle at space point x (in spin state $|\sigma\rangle$) to which all single-particle orbitals ϕ_i contribute. The orbitals are vertically shifted for clarity.

obtain

$$\left[\hat{\psi}(x), \hat{\psi}(x')\right]_\mp = 0, \tag{3.80}$$

$$\left[\hat{\psi}^\dagger(x), \hat{\psi}^\dagger(x')\right]_\mp = 0, \tag{3.81}$$

$$\left[\hat{\psi}(x), \hat{\psi}^\dagger(x')\right]_\mp = \delta(x - x'). \tag{3.82}$$

These relations are straightforwardly proven by direct insertion of the de-

finitions (3.78) and (3.79). We demonstrate this for the last expression:

$$\begin{aligned}\left[\hat{\psi}(x),\hat{\psi}^\dagger(x')\right]_\mp &= \sum_{i,j=1}^{\infty}\phi_i(x)\phi_j^*(x')\left[\hat{a}_i,\hat{a}_j^\dagger\right]_\mp = \\ &= \sum_{i=1}^{\infty}\phi_i(x)\phi_i^*(x') = \delta(x-x') = \delta(\mathbf{r}-\mathbf{r}')\delta_{\sigma,\sigma'},\end{aligned}$$

where, in the last line, we used the representation of the delta function in terms of a complete set of functions.

3.5.2 Representation of operators

We now transform operators into second quantization representation using the field operators, taking advantage of the identical expressions for bosons and fermions.

Single-particle operators

The general second-quantization representation was given by [cf. Secs. 3.3, 3.4]

$$\hat{B}_1 = \sum_{i,j=1}^{\infty}\langle i|\hat{b}|j\rangle a_i^\dagger a_j. \tag{3.83}$$

We now transform the matrix element to coordinate representation:

$$\langle i|\hat{b}|j\rangle = \int dxdx'\phi_i^*(x)\langle x|\hat{b}|x'\rangle\phi_j(x'), \tag{3.84}$$

and obtain for the operator, taking into account the definitions (3.78) and (3.79),

$$\begin{aligned}\hat{B}_1 &= \sum_{i,j=1}^{\infty}\int dxdx'\, a_i^\dagger\phi_i^*(x)\langle x|\hat{b}|x'\rangle\phi_j(x')a_j = \\ &= \int dxdx'\,\hat{\psi}^\dagger(x)\langle x|\hat{b}|x'\rangle\hat{\psi}(x').\end{aligned} \tag{3.85}$$

Diagonal case. For the important case that the matrix is diagonal, $\langle x|\hat{b}|x'\rangle = \hat{b}(x)\delta(x-x')$, the final expression simplifies to

$$\boxed{\hat{B}_1 = \int dx\,\hat{\psi}^\dagger(x)\hat{b}(x)\hat{\psi}(x)} \tag{3.86}$$

Consider a few important examples.

Single-particle density operator. The first example is again the density operator. In first quantization the operator of the particle density for N particles follows from quantizing the classical result for point particles,

$$\hat{n}(x) = \sum_{\alpha=1}^{N} \delta(x - x_\alpha), \tag{3.87}$$

and the expectation value in a certain N-particle state $\Psi(x_1, x_2, \ldots x_N)$ is[25]

$$\begin{aligned} \langle \hat{n} \rangle_\Psi(x) &= \langle\, \Psi | \sum_{\alpha=1}^{N} \delta(x - x_\alpha) | \Psi \,\rangle \\ &= N \int d2d3 \ldots dN |\Psi(x_1 = x, 2, \ldots N)|^2 = n(\mathbf{r}, \sigma), \end{aligned} \tag{3.88}$$

which is the single-particle spin density of a (in general correlated) N-particle system. The *second quantization representation of the density operator* follows from our above result (3.86) by replacing $\hat{b} \to \delta(x - x')$, i.e.

$$\hat{n}(x) = \int dx' \hat{\psi}^\dagger(x') \delta(x - x') \hat{\psi}(x') = \hat{\psi}^\dagger(x) \hat{\psi}(x), \tag{3.89}$$

and the operator of the total density is the sum (integral) over all coordinate-spin states

$$\hat{N} = \int dx\, \hat{n}(x) = \int dx\, \hat{\psi}^\dagger(x) \hat{\psi}(x), \tag{3.90}$$

naturally extending the previous results for a discrete basis to continuous states.

Kinetic energy operator. The second example is the kinetic energy operator which is also diagonal and has the second-quantized representation

$$\hat{T} = \int dx\, \hat{\psi}^\dagger(x) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \hat{\psi}(x). \tag{3.91}$$

The integrand can be understood as (operator of the) kinetic energy density.

Single-particle potential operator. The third example is the second quantization representation of the single-particle potential $v(\mathbf{r})$ given by

$$\hat{V} = \int dx\, \hat{\psi}^\dagger(x) v(\mathbf{r}) \hat{\psi}(x). \tag{3.92}$$

[25] This is the example of an (anti-)symmetrized pure state which is easily extended to mixed states.

If the potential is spin-independent, the spin summation can be performed, and we are left with a coordinate integration.

Note that each of these examples is given by an operator that is a function of the coordinate operator, hence, it is given by a diagonal matrix in coordinate-spin representation.

Two-particle operators

In similar manner we obtain the field operator representation of a general two-particle operator

$$\hat{B}_2 = \frac{1}{2} \sum_{i,j,k,l=1}^{\infty} \langle ij|\hat{b}|kl\rangle a_i^\dagger a_j^\dagger a_l a_k. \tag{3.93}$$

We now transform the matrix element to coordinate representation:

$$\langle ij|\hat{b}|kl\rangle = \int dx_1 dx_2 dx_3 dx_4 \phi_i^*(x_1)\phi_j^*(x_2)\langle x_1 x_2|\hat{b}|x_3 x_4\rangle \phi_l(x_4)\phi_k(x_3), \tag{3.94}$$

and, assuming that the matrix is diagonal,
$\langle x_1 x_2|\hat{b}|x_3 x_4\rangle = \hat{b}(x_1, x_2)\delta(x_1 - x_3)\delta(x_2 - x_4)$, we obtain, after inserting this result into (3.93),

$$\hat{B}_2^{\text{diag}} = \frac{1}{2} \sum_{i,j,k,l=1}^{\infty} \int dx_1 dx_2 \, a_i^\dagger \phi_i^*(x_1) a_j^\dagger \phi_j^*(x_2) \hat{b}(x_1, x_2)\phi_l(x_2) a_l \phi_k(x_1) a_k.$$

Using again the definition of the field operators the final result for a diagonal two-particle operator in coordinate representation is

$$\boxed{\hat{B}_2^{\text{diag}} = \frac{1}{2} \int dx_1 dx_2 \, \hat{\psi}^\dagger(x_1)\hat{\psi}^\dagger(x_2)\hat{b}(x_1, x_2)\hat{\psi}(x_2)\hat{\psi}(x_1)} \tag{3.95}$$

Note again the inverse ordering of the destruction operators which makes this result universally applicable to fermions and bosons. The most important example of this representation is the operator of the two-particle interaction, $\hat{W}$, which is obtained by replacing $\hat{b}(x_1, x_2) \to w(x_1 - x_2)$.

With this, a generic N-particle hamiltonian comprised of kinetic, potential and pair interaction energies becomes, in coordinate representation,

$$\begin{aligned} \hat{H} = &\int dx \, \hat{\psi}^\dagger(x) \left(-\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r}) \right) \hat{\psi}(x) \\ &+ \frac{1}{2} \int dx_1 dx_2 \, \hat{\psi}^\dagger(x_1)\hat{\psi}^\dagger(x_2) w(r_1 - r_2)\hat{\psi}(x_2)\hat{\psi}(x_1) \,, \end{aligned} \tag{3.96}$$

where each integral includes a spin summation: $\int dx \equiv \int d^3r \sum_\sigma$.

Comment: Even though all quantities now depend on a continuous variable $\mathbf{r}$, for practical applications, the coordinate has to be discretized, and the problem is solved on a grid. This may lead to large basis sets, in particular, in non-equilibrium situations where the system is strongly excited. A possible way to optimize the computations is the us of finite element methods (finite element discrete variable representation, FEDVR), e.g. [BBB10a], which we briefly discuss in Sec. 3.7.

3.6 Momentum representation of second quantization operators

We now consider the momentum representation of the creation and annihilation operators. This is useful for translationally invariant systems such as the uniform electron gas (jellium model, cf. Sec. 3.6.3), or, approximately, for dense plasmas, warm dense matter [DGB18], electron-hole plasmas in semiconductors, or nuclear matter, since the eigenfunctions of the momentum operator,

$$\langle x|\phi_{\mathbf{k},s}\rangle = \phi_{\mathbf{k},s}(x) = \frac{1}{\mathcal{V}^{1/2}} e^{i\mathbf{k}\cdot\mathbf{r}} \delta_{s,\sigma}, \quad x = (\mathbf{r},\sigma), \tag{3.97}$$

are eigenfunctions of the translation operator. Here we use periodic boundary conditions to represent an infinite system by a finite box of length L and volume $\mathcal{V} = L^3$, so the wave numbers have discrete values $k_x = 2\pi n_x/L, \dots k_z = 2\pi n_z/L$ with n_x, n_y, n_z being integer numbers. The eigenfunctions (3.97) form a complete orthonormal set, where the orthonormality condition reads

$$\langle \phi_{\mathbf{k},s}|\phi_{\mathbf{k}',s'}\rangle = \frac{1}{\mathcal{V}} \int_{\mathcal{V}} d^3r\, e^{i(\mathbf{k}'-\mathbf{k})\mathbf{r}} \sum_\sigma \delta_{s,\sigma}\delta_{s',\sigma} = \delta_{\mathbf{k},\mathbf{k}'}\delta_{s,s'}, \tag{3.98}$$

and we took into account that the integral over the finite volume $\mathcal{V}$ equals zero, for $\mathbf{k} \neq \mathbf{k}'$, and $\mathcal{V}$, otherwise.

3.6.1 Creation and annihilation operators in momentum space

The creation and annihilation operators on the Fock space of N-particle states constructed from the orbitals (3.97) are obtained by inverting the definition of the field operators (3.78) written with respect to the momentum-spin states (3.97)

$$\hat{\psi}(x) = \sum_{\mathbf{k}'\sigma'} \phi_{\mathbf{k}',\sigma'}(x) \hat{a}_{\mathbf{k}',\sigma'}.$$

Multiplication by $\phi^*_{\mathbf{k},\sigma}(x)$ and integration over x yields, with the help of condition (3.98),

$$\hat{a}_{\mathbf{k},\sigma} = \int dx\, \phi^*_{\mathbf{k}'\sigma'}\hat{\psi}(x) = \frac{1}{\mathcal{V}^{1/2}}\int_{\mathcal{V}} d^3r\, e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{\psi}(\mathbf{r},\sigma), \tag{3.99}$$

and, similarly for the creation operator,

$$\hat{a}^\dagger_{\mathbf{k},\sigma} = \frac{1}{\mathcal{V}^{1/2}}\int_{\mathcal{V}} d^3r\, e^{i\mathbf{k}\cdot\mathbf{r}}\hat{\psi}^\dagger(\mathbf{r},\sigma). \tag{3.100}$$

Relations (3.99) and (3.100) are nothing but the Fourier transforms of the field operators (the same relation as for the coordinate and momentum representations of wave functions). These operators obey the same (anti-)commutation relations as the field operators, which is a consequence of the linear superpositions (3.99), (3.100), cf. the proof of Eq. (3.82).

3.6.2 Representation of operators

We again construct the second quantization representation of the relevant operators, now in terms of creation and annihilation operators in momentum space.

Single-particle operators

For a single-particle operator we have, according to our general result, Eq. (3.70), and denoting $x = (\mathbf{r}, s),\ x' = (\mathbf{r}', s')$,

$$\begin{aligned}
\hat{B}_1 &= \sum_{\mathbf{k}\sigma}\sum_{\mathbf{k}'\sigma'} \hat{a^\dagger}_{\mathbf{k}\sigma}\langle\mathbf{k}\sigma|\hat{b}|\mathbf{k}'\sigma'\rangle\, \hat{a}_{\mathbf{k}'\sigma'} \\
&= \sum_{\mathbf{k}\sigma}\sum_{\mathbf{k}'\sigma'}\int dx\, dx' \hat{a^\dagger}_{\mathbf{k}\sigma}\langle\mathbf{k}\sigma|x\rangle\langle x|\hat{b}|x'\rangle\langle x'|\mathbf{k}'\sigma'\rangle\, \hat{a}_{\mathbf{k}'\sigma'} \\
&= \frac{1}{\mathcal{V}}\sum_{\mathbf{k}\sigma}\sum_{\mathbf{k}'\sigma'}\int dx\, dx' \hat{a^\dagger}_{\mathbf{k}\sigma} e^{-i\mathbf{k}\mathbf{r}}\langle x|\hat{b}|x'\rangle e^{i\mathbf{k}'\mathbf{r}'}\hat{a}_{\mathbf{k}'\sigma'}\delta_{\sigma,s}\delta_{\sigma',s'}, \\
&= \frac{1}{\mathcal{V}}\sum_{\mathbf{k}}\sum_{\mathbf{k}'}\int dx\, dx' \hat{a^\dagger}_{\mathbf{k}s} e^{-i\mathbf{k}\mathbf{r}}\langle x|\hat{b}|x'\rangle e^{i\mathbf{k}'\mathbf{r}'}\hat{a}_{\mathbf{k}'s'},
\end{aligned} \tag{3.101}$$

where, in the third line, we inserted complete sets of momentum eigenstates (3.97). If the momentum matrix elements of the operator $\hat{b}$ are known, the first line can be used directly. Otherwise, the matrix element is obtained from the known coordinate space result in the last line.

Kinetic energy. For an operator that commutes with the momentum operator and, thus, is given by a diagonal matrix, one integration (and spin summation) can be performed. We demonstrate this for the example of the kinetic energy operator. Then $\langle x|\hat{b}|x'\rangle \to -\frac{\hbar^2\nabla^2}{2m}\delta(x-x')$, and we obtain from (3.101), using the orthonmoramlity property (3.98),

$$\begin{aligned}\hat{T} &= \frac{1}{\mathcal{V}}\sum_{\mathbf{k}\sigma}\sum_{\mathbf{k}'}\hat{a^\dagger}_{\mathbf{k}\sigma}\hat{a}_{\mathbf{k}'\sigma}\int_{\mathcal{V}} d^3r\; e^{-i\mathbf{k}\mathbf{r}}\,\frac{\hbar^2 k'^2}{2m}\,e^{i\mathbf{k}'\mathbf{r}} \\ &= \sum_{\mathbf{k}\sigma}\frac{\hbar^2\mathbf{k}^2}{2m}\hat{a^\dagger}_{\mathbf{k}\sigma}\hat{a}_{\mathbf{k}\sigma}. \end{aligned} \tag{3.102}$$

Note that one spin summation remains of the two that are contained in the x-integrals in Eq. (3.101) [the second is removed due to the diagonality of $\hat{b}$].

Single-particle potential. In similar fashion we obtain for the single-particle potential, upon replacing $\langle x|\hat{b}|x'\rangle \to v(\mathbf{r})\delta(x-x')$,

$$\begin{aligned}\hat{V} &= \sum_{\mathbf{k}\sigma}\sum_{\mathbf{k}'}\hat{a^\dagger}_{\mathbf{k}\sigma}\,\hat{a}_{\mathbf{k}'\sigma}\frac{1}{\mathcal{V}}\int_{\mathcal{V}} d^3r\, e^{-i\mathbf{k}\mathbf{r}}\,v(\mathbf{r})\,e^{i\mathbf{k}'\mathbf{r}} \\ &= \sum_{\mathbf{k}\sigma}\sum_{\mathbf{k}'}\tilde{v}_{\mathbf{k}-\mathbf{k}'}\hat{a^\dagger}_{\mathbf{k}\sigma}\,\hat{a}_{\mathbf{k}'\sigma}, \end{aligned} \tag{3.103}$$

where we introduced the Fourier transform of the single-particle potential, $\tilde{v}_{\mathbf{q}} \equiv \mathcal{V}^{-1}\int d^3r\, v(\mathbf{r})e^{-i\mathbf{q}\mathbf{r}}$. Note that the single-particle potential operator is not given by a diagonal matrix, and it is not expressed in terms of orbital occupations, $\hat{n}_{k\sigma}$. This is, of course, a direct consequence of non-commutativity of coordinate and momentum. In other words, the space dependence $v(\mathbf{r})$ breaks the translational invariance of the system.

Single-particle density. Finally, the operator of the single-particle density becomes, in momentum space by Fourier transformation,

$$\begin{aligned}\hat{n}_{\mathbf{q}} &= \sum_{\sigma}\hat{n}_{\mathbf{q}\sigma} = \sum_{\sigma}\frac{1}{\mathcal{V}}\int_{\mathcal{V}} d^3r\,\hat{\psi}^\dagger_\sigma(\mathbf{r})\hat{\psi}_\sigma(\mathbf{r})\,e^{-i\mathbf{q}\mathbf{r}} \\ &= \frac{1}{\mathcal{V}}\sum_{\sigma\mathbf{k}\mathbf{k}'}\hat{a}^\dagger_{\mathbf{k}'\sigma}\hat{a}_{\mathbf{k}\sigma}\,\frac{1}{\mathcal{V}}\int_{\mathcal{V}} d^3r\, e^{i(\mathbf{k}-\mathbf{k}')\mathbf{r}}e^{-i\mathbf{q}\mathbf{r}} \\ &= \frac{1}{\mathcal{V}}\sum_{\sigma\mathbf{k}}\hat{a}^\dagger_{\mathbf{k}-\mathbf{q},\sigma}\hat{a}_{\mathbf{k}\sigma}. \end{aligned} \tag{3.104}$$

This shows that the Fourier component of the single-particle density operator, $\hat{n}_{\mathbf{q}}$, describes a *density fluctuation* with wave number $\mathbf{q}$, corresponding to

transitions of the particles from state $|\phi_{\mathbf{k}\sigma}\rangle$ to state $|\phi_{\mathbf{k}-\mathbf{q},\sigma}\rangle$, for arbitrary $\mathbf{k}$. With this result we may rewrite the single-particle potential (3.103) as

$$\hat{V} \;=\; \mathcal{V}\sum_{\mathbf{q}} \tilde{v}_{\mathbf{q}}\, \hat{n}_{-\mathbf{q}}. \tag{3.105}$$

Two-particle operators

We now turn to two-particle operators. Rewriting the general result (3.74) for a spin-momentum basis, we obtain

$$\hat{B}_2 = \frac{1}{2!}\sum_{\mathbf{k}_1\sigma_1\mathbf{k}_2\sigma_2}\sum_{\mathbf{k}_1'\sigma_1'\mathbf{k}_2'\sigma_2'} \hat{a^\dagger}_{\mathbf{k}_1\sigma_1}\hat{a^\dagger}_{\mathbf{k}_2\sigma_2}\left\langle \mathbf{k}_1\sigma_1\mathbf{k}_2\sigma_2\right|\hat{b}\left|\mathbf{k}_1'\sigma_1'\mathbf{k}_2'\sigma_2'\right\rangle \hat{a}_{\mathbf{k}_2'\sigma_2'}\hat{a}_{\mathbf{k}_1'\sigma_1'}\,. \tag{3.106}$$

We now apply this result to the interaction potential where the matrix element in momentum representation was computed before,

$$\langle \mathbf{k}_1\sigma_1\mathbf{k}_2\sigma_2|\hat{w}|\mathbf{k}_1'\sigma_1'\mathbf{k}_2'\sigma_2'\rangle = \tilde{w}(\mathbf{k}_1-\mathbf{k}_1')\delta_{\mathbf{k}_1+\mathbf{k}_2,\mathbf{k}_1'+\mathbf{k}_2'}\delta_{\sigma_1,\sigma_1'}\delta_{\sigma_2,\sigma_2'}. \tag{3.107}$$

Here $\tilde{w}$ denotes the Fourier transform of the pair interaction, and the interaction does not change the spin of the involved particles, see problem 6, Sec. 3.9. Inserting this into Eq. (3.106) and introducing the momentum transfer $\mathbf{q} = \mathbf{k}_1' - \mathbf{k}_1 = \mathbf{k}_2 - \mathbf{k}_2'$, we obtain

$$\hat{W} \;=\; \frac{1}{2!}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{q}}\sum_{\sigma_1\sigma_2}\tilde{w}(q)\hat{a^\dagger}_{\mathbf{k}_1\sigma_1}\hat{a^\dagger}_{\mathbf{k}_2\sigma_2}\hat{a}_{\mathbf{k}_2-\mathbf{q},\sigma_2}\hat{a}_{\mathbf{k}_1+\mathbf{q},\sigma_1}\,. \tag{3.108}$$

In the case of a Coulomb potential, the contribution of $q = 0$ is divergent and should be excluded (this will be discussed below in Sec. 3.6.3). In similar manner other two-particle quantities are computed.

With this result we can write down the second quantization representation in spin-momentum space of a generic many-particle hamiltonian that contains kinetic energy, an external potential and a pair interaction contribution. From the expressions (3.102, 3.103, 3.108) we obtain

$$\begin{aligned}\hat{H} \;=\; & \sum_{\mathbf{k}\sigma}\frac{\hbar^2k^2}{2m}\,\hat{a^\dagger}_{\mathbf{k}\sigma}\hat{a}_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\mathbf{k}'\sigma}\tilde{v}_{\mathbf{k}-\mathbf{k}'}\,\hat{a^\dagger}_{\mathbf{k}\sigma}\hat{a}_{\mathbf{k}'\sigma} \\ & + \frac{1}{2!}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{q}}\sum_{\sigma_1\sigma_2}\tilde{w}(q)\hat{a^\dagger}_{\mathbf{k}_1\sigma_1}\hat{a^\dagger}_{\mathbf{k}_2\sigma_2}\hat{a}_{\mathbf{k}_2-\mathbf{q},\sigma_2}\hat{a}_{\mathbf{k}_1+\mathbf{q},\sigma_1}\,.\end{aligned} \tag{3.109}$$

This result is a central starting point for many investigations in condensed matter physics, quantum plasmas or nuclear matter. We will apply this result

to one of the key model systems – the uniform electron gas ("jellium") – in Sec. 3.6.3.

Finally, let us compare this result to the coordinate representation. In both cases the kinetic energy part is diagonal. However, the coordinate representation contains a complicated differential operator whereas the momentum representation includes just a factor k^2. On the other hand, the momentum representation of the interaction potential is more complicated than in the coordinate representation. While in the latter we have two sums (integrals) over the orbitals (coordinates), in the former case there are three. Therefore, the momentum representation will be advantageous if kinetic energy dominates (weakly coupled quantum system) and, vice versa, in the strong coupling limit.

3.6.3 The uniform electron gas (jellium)

An important special case where the momentum representation is advantageous is the uniform electron gas (UEG) or jellium. This is a key model system in many-body and condensed matter physics as it allows to describe fundamental properties of quantum degenerate electrons including their long-range Coulomb interaction. To restore charge neutrality one includes a charge compensating background. The assumption of the model is that this background is uniform and static and does not respond to the dynamics of the electrons. This background compensates the divergent term with $q = 0$ in the electron-electron interaction.

The uniform electron gas is spatially homogeneous, so the momentum is conserved. The hamiltonian of this system follows from the result (3.109) by omitting the external potential,

$$\begin{aligned} \hat{H} &= \sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m} \hat{a^\dagger}_{\mathbf{k}\sigma} \hat{a}_{\mathbf{k}\sigma} + E_M \\ &\quad + \frac{1}{2!} {\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{q}}}' \sum_{\sigma_1\sigma_2} \tilde{w}(q) \hat{a^\dagger}_{\mathbf{k}_1\sigma_1} \hat{a^\dagger}_{\mathbf{k}_2\sigma_2} \hat{a}_{\mathbf{k}_2-\mathbf{q},\sigma_2} \hat{a}_{\mathbf{k}_1+\mathbf{q},\sigma_1} \ , \end{aligned} \tag{3.110}$$

where the Madelung energy accounts for the selfinteraction of the ions (derived from the Ewald procedure) and is given by [SGVB15]
$E_M = -2.837297 \left(\frac{3}{4\pi}\right)^{1/3} \frac{N^{2/3}}{r_s}$. Furthermore, the prime on the sum indicates that the $q = 0$ term is missing in the sum over $\mathbf{q}$. This is motivated by the fact that, in reality, the charge of the electron gas is compensated by the ionic background. In the jellium model this background is assumed to be purely static.