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.

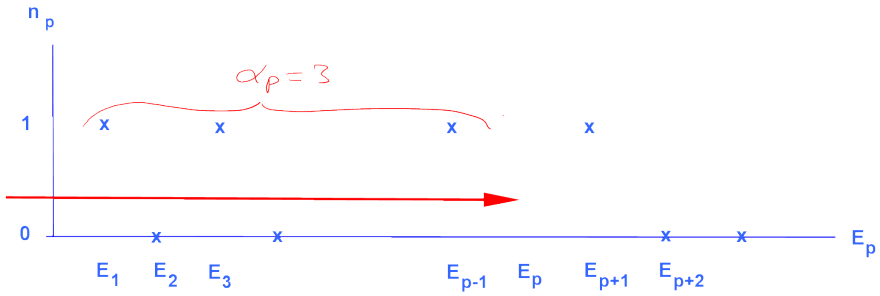

Abbildung 3.6: Illustration of the phase factor α in the fermionic creation and annihilation operators. A fermion is added to orbital "p" (red arrow) and has to be moved past three singly occupied orbitals ($n_p = 1$) with lower energy. This requires $\alpha_p = 3$ pair exchanges, i.e. a sign change 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

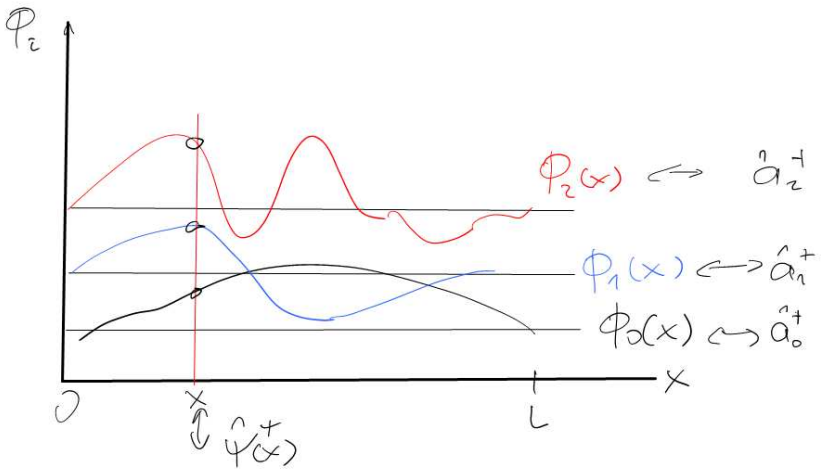

Abbildung 3.7: Illustration of the relation of the field operators to the second quantization operators defined on a general basis $\{\phi_i(x)\}$. The field operator $\hat{\psi}^\dagger(x)$ creates a particle at space point x (in spin state $|\sigma\rangle$) to which all single-particle orbitals ϕ_i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

The thermodynamic properties of the UEG and the main idea of CPIMC will be discussed in Sec. 4.3.

Application to relativistic quantum systems

The momentum representation is conveniently extended to relativistic many-particle systems. In fact, since the Dirac equation of a free particle has plane wave solutions, we may use the same single-particle orbitals as in the non-relativistic case. With this, the matrix elements of the single-particle potential and of the interaction potential remain unchanged (if magnetic corrections to the interaction are neglected). The only change is in the kinetic energy contribution, due to the relativistic modification of the single-particle dispersion, $\epsilon_k = \frac{\hbar^2 k^2}{2m} \to \sqrt{\hbar^2 k^2 c^2 + m^2 c^4}$, where m is the rest mass. In the ultra-relativistic limit, $\epsilon_k = \hbar c k$. Otherwise the hamiltonian (3.109) remains valid.

Of course, this is true only as long as pair creation processes are negligible. Otherwise we would need to extend the description by introducing the negative energy branch $\epsilon_{k-} = -\sqrt{\hbar^2 k^2 c^2 + m^2 c^4}$ and the corresponding second set of plane wave states. In all matrix elements we would need to include a second index $(+, -)$ referring to the energy band. For interacting systems, furthermore, relativistic corrections to the interaction energy have to be included.

3.7 Other basis sets

In the sections above we derived the second quantization representation of many-particle states and operators. We derived the results for a general representation in a complete orthonormal system of orbitals $\{|i\rangle\}$ and for two specific representations: the coordinate and momentum representations. The solution of the problem becomes trivial if the hamiltonian is diagonal in the chosen representation.

System in an external potential. If the particles are exposed to a single-particle potential such as a Coulomb potential of a nucleus or an oscillator potential, use of the momentum representation is not advantageous because the external potential is not diagonal in momentum eigenstates. In that case the eigenstates of a single particle in that potential, such as the hydrogen wave functions or the oscillator eigenstates, allow for an efficient description. Alternatively problems in an external potential can be solved on a coordinate grid, i.e. in coordinate representation because there potential energy operators are diagonal. However, coordinate grids can become very large. This problem can be reduced by choosing, instead of a Cartesian system properly adapted

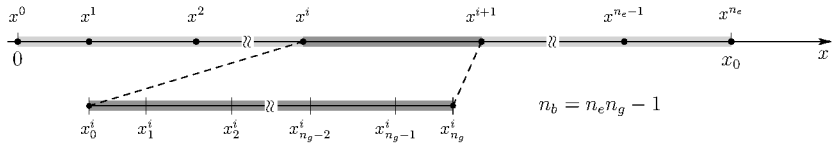

Abbildung 3.8: In an FE-DVR representation, the interval $[0, x_0]$ is partitioned into n_e finite elements $[x_i, x_{i+1}]$. In each FE, n_g generalized Gauss-Lobatto points (denoted x^i_m) provide the basis for the construction of a local DVR basis set; n_b denotes the dimensionality of the extended basis covering the whole interval. From Ref. [BBB10a].

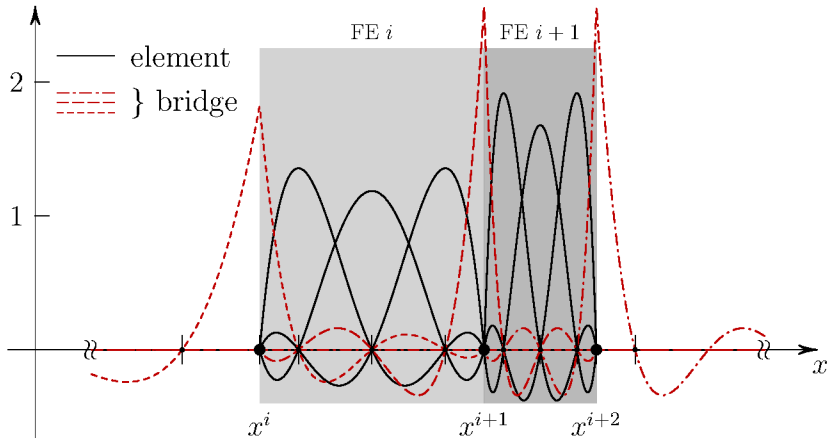

Abbildung 3.9: Structure of a FE-DVR basis $\{\chi^i_m(x)\}$ with $n_g = 4$ (i.e., five local DVR basis functions in each element). While the element functions (solid) are defined in a single FE, the bridge functions (dashed and dashed-dotted lines) link two adjacent FEs. From Ref. [BBB10a].

coordinate systems, such as spherical coordinates (for single-center potentials) or prolate spheroidal basis (for two-atomic molecules), e.g. [LBSB16].

Combination of grid and basis representations. The size of a coordinate grid can be further reduced by making the grid non-equidistant or adaptive and time-dependent. An alternative approach is a combination of grid and basis expansions – the so-called finite element discrete variable representation (FEDVR). Here the space is divided into a set of finite elements FE which can be non-equidistant. Inside of each finite element, a basis set $\{\chi^i_m(x)\}$ is introduced which allows for a compact representation of functions within the interval and for efficient space integrations. A one-dimensional example for the grid is shown in Fig. 3.8, and the functions in two adjacent finite elements are illustrated in Fig. 3.9. The main advantage is that second quantization

operators retain the same properties as in the standard coordinate representation, in particular the diagonality of all potential terms. This method has been applied for solutions of the time-dependent Schrödinger equation, as well as for the propagation of the Keldysh-Kadanoff-Baym equations of Nonequilibrium Green Functions theory, for the latter see Refs. [BBB10a, BBB10b]. For applications to three-dimensional atomic systems, often a radial FEDVR is used, combined with spherical harmonics, for the angular part. For details and further references, see the review [HHB14].

Interacting particles. On the other hand, in the case of interactions between the particles, the matrix representation of the pair interaction operator is the main bottleneck. If the interaction is weak an accurate representation of the single-particle hamiltonian including the external potential is important, and the use of the eigenfunctions of the single-particle hamiltonian is appropriate. In contrast, if the pair interaction is strong it may be advantageous to use basis states that, at least partially, take into account interaction effects. This can be obtained from an approximate solution of the interacting problem. A popular approach is to treat the many-body system on the mean field level and use Hartree or Hartree-Fock eigenstates for which efficient numerical procedures have been developed. In that case the total hamiltonian is brought to the form

$$\hat{H} = \hat{H}_1 + \hat{W}^{\mathrm{MF}} + \hat{W}^{\mathrm{corr}} \tag{3.111}$$

and the Hartree or Hartree-Fock eigenstates diagonalize the first two terms. The complexity of the problem then depends on the properties of the matrix elements of the remaining interactions, i.e. of the correlation part of the hamiltonian and the approximations used for its treatment.

Optimized basis sets. For completeness we mention that there exist various basis sets that are optimized for specific applications and make a compromise between accuracy and computational efficiency. For example, in quantum chemistry, for the description of atoms and molecules, often instead of the exact hydrogen-type orbitals simpler functions are used, such as Slater-type or Gaussian-type orbitals, see e.g. our discussion in Sec. 3.2.5. In density functional theory, on the other hand, often pseudopotentials are used or combinations of localized states in the vicinity of atoms or ions and plane waves in the outer region, for a text book discussion, see Ref. [Mar12]. Similar approaches are used in atomic and molecular physics in the context of restricted active space methods, see Sec. 3.2.5.