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 difference being the details of the commutation (anticommutation) rules of the respective creation and annihilation operators. 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 definitions (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:

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

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

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

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.

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]

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

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

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

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

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

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

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),

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

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

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

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 $k_x = 2\pi n_x/L, \ldots k_z = 2\pi n_z/L$ 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. 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 $x = (\mathbf{r}, s),\ x' = (\mathbf{r}', s')$,

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

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, using the property (3.98),

$$\begin{aligned}
\hat{T} &= \frac{1}{\mathcal{V}}\sum_{\mathbf{k}\sigma}\sum_{\mathbf{k}'}\int_{\mathcal{V}} d^3r\, a^\dagger_{\mathbf{k}\sigma}\, e^{-i\mathbf{k}\mathbf{r}}\,\frac{\hbar^2 k'^2}{2m}\, e^{i\mathbf{k}'\mathbf{r}} a_{\mathbf{k}'\sigma} \\
&= \sum_{\mathbf{k}\sigma}\frac{\hbar^2\mathbf{k}^2}{2m} a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}. \qquad (3.102)
\end{aligned}$$

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 $\langle x|\hat{b}|x'\rangle \to v(\mathbf{r})\delta(x-x')$,

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

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,

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

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

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

We now apply this result to the interaction potential where the matrix element in momentum representation was computed before, $\langle \mathbf{k}_1\sigma_1\mathbf{k}_2\sigma_2|\hat{w}|\mathbf{k}'_1\sigma'_1\mathbf{k}'_2\sigma'_2\rangle =$

$\tilde{w}(\mathbf{k}_1 - \mathbf{k}_1')\delta_{\mathbf{k}_1+\mathbf{k}_2,\mathbf{k}_1'+\mathbf{k}_2'}\delta_{\sigma_1,\sigma_1'}\delta_{\sigma_2,\sigma_2'}$. 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

$$\hat{W} = \frac{1}{2!}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{q}}\sum_{\sigma_1\sigma_2}\tilde{w}(q)a^\dagger_{\mathbf{k}_1\sigma_1}a^\dagger_{\mathbf{k}_2\sigma_2}a_{\mathbf{k}_2-\mathbf{q},\sigma_2}a_{\mathbf{k}_1+\mathbf{q},\sigma_1}\ . \tag{3.107}$$

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, 3.107) we obtain

$$\begin{aligned}\hat{H} &= \sum_{\mathbf{k}\sigma}\frac{\hbar^2k^2}{2m}\,a^\dagger_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\mathbf{k}'\sigma}\tilde{v}_{\mathbf{k}-\mathbf{k}'}\,a^\dagger_{\mathbf{k}\sigma}a_{\mathbf{k}'\sigma} \\ &\quad + \frac{1}{2!}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{q}}\sum_{\sigma_1\sigma_2}\tilde{w}(q)a^\dagger_{\mathbf{k}_1\sigma_1}a^\dagger_{\mathbf{k}_2\sigma_2}a_{\mathbf{k}_2-\mathbf{q},\sigma_2}a_{\mathbf{k}_1+\mathbf{q},\sigma_1}\ .\end{aligned} \tag{3.108}$$

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 (3.108) by omitting the external potential,

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

where the Madelung energy accuonts for the selfinteractio 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 the 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 (3.108) 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 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

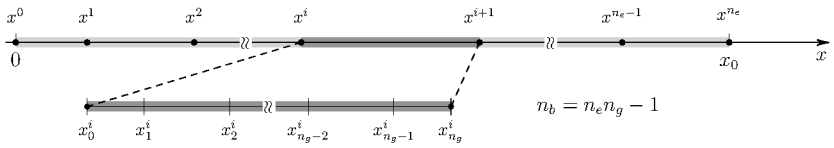

Abbildung 3.8: In an FE-DVR representation, the interval $[0, x_0]$ is partitioned into n_e finite elements $[x_i, x_{i+1}]$. In each FE, n_g generalized Gauss-Lobatto points (denoted x_m^i) provide the basis for the construction of a local DVR basis set; n_b denotes the dimensionality of the extended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

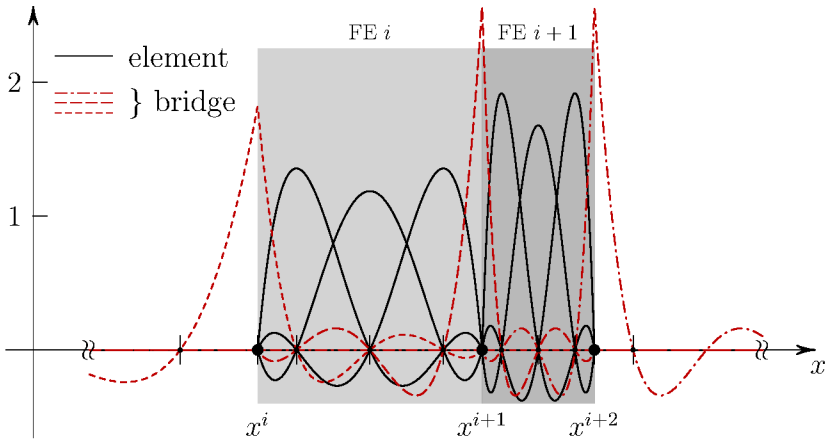

Abbildung 3.9: Structure of a FE-DVR basis $\{\chi_m^i(x)\}$ with $n_g = 4$ (i.e., five local DVR basis functions in each element). While the element functions (solid) are defined in a single FE, the bridge functions (dashed and dashed-dotted lines) link two adjacent FEs. From Ref. [BBB10a].

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

$$\hat{H} = \hat{H}_1 + \hat{W}^{\mathrm{MF}} + \hat{W}^{\mathrm{corr}} \tag{3.110}$$

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.

3.8 Observables. Expectation values.

For practical applications and comparison with experiments we need to go beyond the representation of many-particle states or of operators. What is needed is to compute expectation values of operators in the proper state of the system. Examples are the total energy, the interaction energy, the dipole moment or the optical absorption spectrum. This problem is well understood for simple

systems such as the hydrogen atom. There the energy in a given state $|nlm\rangle$ reduces to the computation of the expectation value, $\langle \hat{H} \rangle = \langle nlm|\hat{H}|nlm\rangle = E_n$, whereas the dipole absorption spectrum is related to matrix elements of the dipole operator, $\langle nlm|\hat{P}|n'l'm'\rangle$, leading to the well-known dipole selection rules. However, these properties become already much more complicated if more than one electron is involved, such as in helium, lithium or more complex atoms or molecules. In this case, the proper spin (anti-)symmetry has to be taken into account in the computation of the expectation value.

3.8.1 (Anti-)symmetrized observables of many-particle systems

To compute the expectation value of an operator $\hat{A}$ in a pure state we have to use the (anti-)symmetrized version of the latter, given by Eq. (3.13),

$$\langle \hat{A} \rangle^{\pm} = \langle \{n\}|\hat{A}|\{n\}\rangle = \tag{3.111}$$

$$= \langle \Psi_{\{j\}} \Lambda^{\pm}_{1\ldots N} |\hat{A}| \Lambda^{\pm}_{1\ldots N} \Psi_{\{j\}} \rangle = \langle \Psi_{\{j\}}|\hat{A}^{\pm}|\Psi_{\{j\}}\rangle \,, \tag{3.112}$$

where, in the last line, we expressed the result in terms of non-(anti-)symmetric N-particle states whereas the (anti-)symmetrization is carried over to the operator, $\hat{A} \to \hat{A}^{\pm} = \Lambda^{\pm}_{1\ldots N} \hat{A} \Lambda^{\pm}_{1\ldots N}$. Of course, both results are identical. Below we consider them separately.

3.8.2 Expectation values with product states

Let us start by considering the second version of the computation of expectation values given by Eq. (3.112). Then the states can be represented as linear superpositions of product states, $|\Psi_{\{j\}} = |j_1\rangle \ldots |j_N\rangle$ leading to comparatively simple integrations or summations. Still we need to work out the (anti-)symmetrization of the involved operator. We illustrate this for a two-particle system. Then we can transform

$$\hat{A}^{\pm}_{12} = \Lambda^{\pm}_{12} \hat{A}_{12} \Lambda^{\pm}_{12} =$$

$$= \hat{A}_{12} \left(\Lambda^{\pm}_{12}\right)^2 = \tag{3.113}$$

$$= \hat{A}_{12} \lambda^{\pm}_{12} \tag{3.114}$$

$$\lambda^{\pm}_{1\ldots N} = (N!)^{1/2} \Lambda^{\pm}_{1\ldots N} \,, \tag{3.115}$$

where we defined a modified (anti-)symmetrization operator in order to eliminate the normalization factor. For example, $\lambda^{\pm}_{12} = 1 \pm P_{12}$. Let us first verify the second line, Eq. (3.113), which implies that $[\Lambda^{\pm}_{12}, \hat{A}_{12}] = 0$. This commutator

is easily computed by using the matrix representation of the involved operators with respect to an arbitrary complete orthonormal system of two-particle states,

$$\begin{aligned}\sqrt{2}\,\langle i_1 i_2|[\Lambda^{\pm}_{12}, \hat{A}_{12}]|j_1 j_2\rangle &= \sum_{k_1 k_2} \{\langle i_1 i_2|k_1 k_2\rangle \pm \langle i_1 i_2|k_2 k_1\rangle\}\,\langle k_1 k_2|\hat{A}|j_1 j_2\rangle \\ &\quad - \sum_{k_1 k_2} \langle i_1 i_2|\hat{A}|k_1 k_2\rangle\,\{\langle k_1 k_2|j_1 j_2\rangle \pm \langle k_2 k_1|j_1 j_2\rangle\} \\ &= \pm\Big\{\langle i_2 i_1|\hat{A}|j_1 j_2\rangle - \langle i_1 i_2|\hat{A}|j_2 j_1\rangle\Big\}\,, \qquad (3.116)\end{aligned}$$

where the direct terms cancel and, in the exchange terms, we used the orthonormality, $\langle j|i\rangle = \delta_{ij}$. We conclude that the commutator vanishes if $\langle i_1 i_2|\hat{A}|j_1 j_2\rangle = \langle i_2 i_1|\hat{A}|j_2 j_1\rangle$, i.e. for an operator that is symmetric in the particle indices, $A_{12} = A_{21}$, which is an expected property for identical particles.

Square of the (anti-)symmetrization operators. Now it remains to prove relation (3.114) which we demonstrate by explicit calculation,

$$\big(\lambda^{\pm}_{12}\big)^2 = (\hat{1} \pm \hat{P}_{12})(\hat{1} \pm \hat{P}_{12}) = 2(\hat{1} \pm \hat{P}_{12}) = 2\lambda^{\pm}_{12}\,.$$

Similarly one readily confirms[26] that $\big(\lambda^{\pm}_{123}\big)^2 = 6\lambda^{\pm}_{123}$. This can be generalized to the result

$$\big(\lambda^{\pm}_{1\ldots s}\big)^2 = s!\,\lambda^{\pm}_{1\ldots s} \qquad (3.117)$$

$$\big(\Lambda^{\pm}_{1\ldots s}\big)^2 = (s!)^{1/2}\,\Lambda^{\pm}_{1\ldots s} = \lambda^{\pm}_{1\ldots s} \qquad (3.118)$$

The fact that the square of the operators can be reduced to the first power is not surprising since $\Lambda^{\pm}_{12}$ projects onto the (anti-)symmetric subspace of the two-particle Hilbert space and, repeating this operation once more (or more than once), will not change the result, up to a coefficient. The same is true for the case of $N \geq 3$. This and more properties of the (anti-)symmetrization operators will be investigated in more detail in Sec. 6.6.3.

Summary. To summarize the result of this section, we have shown that expectation values for fermions and bosons can be computed using states that are not (anti-)symmetrized. Instead, the observable A needs to be (anti-)symmetrized by computing $\hat{A}^{\pm} = \hat{A}\lambda^{\pm}$. In practice this means that the matrix representation has to be replaced by (for $N = 2$)

$$\begin{aligned}\langle i_1 i_2|\hat{A}_{12}|j_1 j_2\rangle \to \langle i_1 i_2|\hat{A}_{12}|j_1 j_2\rangle \pm \langle i_1 i_2|\hat{A}_{12}|j_2 j_1\rangle = \\ = \langle i_1 i_2|\hat{A}_{12}|j_1 j_2\rangle \pm \langle i_2 i_1|\hat{A}_{12}|j_1 j_2\rangle\,.\end{aligned}$$

[26] See problems, Sec. 3.9

An example where this is used is the pair potential w_{12} which is often replaced by $w_{12}^{\pm}$. The main advantage of doing this is that the number of particle pairs contributing to the total interaction energy $\hat{W}$ can be reduced, see Sec. 3.10.8.

Further examples of (anti-)symmetrized operators are the reduced density operators, $F_{12}^{\pm}$, $F_{123}^{\pm}$ and so on, see Chapter 6, and nonequilibrium Green functions, see Chapter 8. For these approaches, therefore, representations in terms of product states are commonly used. The properties of the (anti-)symmetrization operators will be studied in more detail in Sec. 6.6.1.

3.8.3 Expectation values with (anti-)symmetric states

Let us now turn to the computation of expectation values in terms of Slater determinants/permanents. As an example we consider a system without interaction for which the hamiltonian is additive,

$$\hat{H} = \sum_{i,j=1}^{\infty} h_{ij}\, a_i^\dagger a_j \,, \tag{3.119}$$

with the matrix elements $\langle\{n\}|\hat{H}|\{n'\}\rangle$. If the system is spatially uniform, it is advantageous to use the momentum representation with the hamiltonian in the form (3.108). Occupation number states are then Slater determinants or permanents of plane waves which are eigenstates of the hamiltonian which is given by the unitary product with identical vectors,

$$\langle\{n\}|\sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m}\, a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma}|\{n'\}\rangle = \sum_{\mathbf{k}\sigma} \frac{\hbar^2 k^2}{2m}\, n_{\mathbf{k}\sigma}\delta_{\{n\},\{n'\}} \,. \tag{3.120}$$

Obviously, this hamiltonian is diagonal in the Fock state basis and on the diagonal appear the eigenvalues of the total single particle energy, i.e. the total energy, in the given N-particle state.

Expectation value of single-particle operators. Let us now repeat this procedure for an arbitrary single-particle operator $\hat{B}_1$ in a general basis and compute the expectation value of this operator in a given Fock state. To this end we only need the diagonal matrix element,

$$\begin{aligned}
\langle\hat{B}_1\rangle = \langle\{n\}|\hat{B}_1|\{n\}\rangle &= \langle\{n\}|\sum_{i,j=1}^{\infty} b_{ij}\, a_i^\dagger a_j|\{n\}\rangle \\
&= \sum_{i,j=1}^{\infty} \delta_{ij} b_{ij}\, \langle\{n\}|a_i^\dagger a_j|\{n\}\rangle \\
&= \sum_{i=1}^{\infty} b_{ii}\, n_i \,,
\end{aligned} \tag{3.121}$$

where n_i are the occupation numbers in the state $|\{n\}\rangle$, and only the diagonal elements of b_{ij} give a non-vanishing contribution. Obviously, if Slater determinants or permanents are used it is advantageous to employ the second quantization representation of the observable, because the action of the creation and annihilation operators on the states can be straightforwardly computed.

Expectation values for stationary solutions of the Schrödinger equation. The expectation value (3.121) holds for any Slater determinant/permanent constructed from eigenstates of the single-particle hamiltonian, i.e. of the one-particle Schrödinger equation. This can be a uniform system (then we would use plane waves) or a system in an external potential – then we would use the eigenfunctions of the hamiltonian in that potential.

In contrast, if the system is interacting and is described by the complete hamiltonian (3.108), the interaction term is highly non-diagonal in a plane wave basis. The exact solution procedure then corresponds to a diagonalization of this hamiltonian. This is always possible – at least, in principle – and leads to the so-called *natural orbitals*. If these orbitals are found the hamiltonian is again additive, as in the case above. However, this diagonalization procedure scales exponentially with the number of single-particle orbitals needed to represent the system which makes exact solutions impractical already for small particle numbers on the order of $N = 20 \ldots 30$, see our discussion in Sec. 3.2.5.

Due to this difficulty of exact diagonalization, alternative methods to solve the many-body ground state problem have been developed which include perturbation theory or variational approaches. A different route are computational approaches such as density functional theory (DFT), many-body perturbation theory, and quantum Monte Carlo (QMC). For systems in the ground state the most advanced methods are diffusion Monte Carlo (DMC) and full configuration interaction QMC (FCIQMC), the former operating in coordinate space and the latter in Slater determinant space which was developed by A. Alavi and co-workers. Here we will not further explore ground state approaches but refer to the extensive literature on DMC and FCIQMC in physics and quantum chemistry. Instead, we will consider in more detail the case of finite temperatures, cf. chapter 4.

3.8.4 Outlook

After investigating the basic properties of the method of second quantization we now turn to more advanced topics. One of them is the extension of the analysis to systems at a finite temperature, i.e. in a mixed ensemble. This will be the subject of Chapter 4. After this we turn to the time evolution of the field operators following an external perturbation. This will be studied in

detail for the case of single-time observables, in Chapter 5. A second route to nonequilibrium dynamics is to use field operator products that depend on two times which leads to the theory of nonequilibrium Green functions which we discuss in Chapter 8.

3.9 Problems to Chapter 3

1. Express $\lambda^{\pm}_{123}$ via $\lambda^{\pm}_{12}$ and $\Lambda^{\pm}_{123}$ via $\Lambda^{\pm}_{12}$, cf.

2. Generalize the previous result to find a decomposition of $\lambda^{\pm}_{1\ldots N}$ into lower order operators.

3. Prove the bosonic commutation relations (3.35).

4. Prove the anti-commutation relation (3.64) between fermionic creation and annihiliation operators.

5. Discuss what happened to the sum over α in the derivation of Eq. (3.49).

6. Compute the momentum matrix element of the pair interaction.

7. Prove that $\left(\Lambda^{\pm}_{123}\right)^2 = (3!)^{1/2}\Lambda^{\pm}_{123}$

3.10 Supplement: Matrix elements in Fock space. Spinor representation for fermions

We now further extend the analysis of the anti-symmetric Fock space. A convenient orthonormal basis for a system of N fermions are the anti-symmetric states[27] $|\{n\}\rangle$, cf. Eq. (3.21). Then operators are completely defined by their action on these states and by their matrix elements. For fermions the occupation number representation can be cast into a simple spinor formulation which we consider next.

3.10.1 Spinor representation of single-particle states

The fact that the fermionic occupation numbers have only two possible values is very similar to the two spin projections of spin-1/2 particles and allows

[27] This representation is being used, e.g., in quantum Monte Carlo simulations, such as configuration path integral Monte Carlo, cf. Ref. [SBF+11]

for a very intuitive description in terms of spinors. Thus, an empty or singly occupied orbital can be written as a column

$$|0\rangle \to \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad - \quad \text{empty orbital,}$$
$$|1\rangle \to \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad - \quad \text{occupied orbital,}$$

and, analogously for the "bra"-states,

$$\langle 0| \to \begin{pmatrix} 1 & 0 \end{pmatrix} \quad - \quad \text{empty orbital,}$$
$$\langle 1| \to \begin{pmatrix} 0 & 1 \end{pmatrix} \quad - \quad \text{occupied orbital,}$$

where the two form an orthonormal basis: $\langle 0|0\rangle = \langle 1|1\rangle = 1$; $\langle 0|1\rangle = 0$. We will also use the combined notation $\langle \alpha|\beta\rangle = \delta_{\alpha,\beta}$, where $\alpha, \beta = 0, 1$.

3.10.2 Spinor representation of operators

In the spinor representation each second quantization operator becomes a 2×2 matrix,

$$\hat{A} \to A_{\alpha\beta} = \begin{pmatrix} A_{00} & A_{01} \\ A_{10} & A_{11} \end{pmatrix}, \tag{3.122}$$

where $A_{\alpha\beta} = \langle \alpha|\hat{A}|\beta\rangle$ and $\alpha, \beta = 0, 1$.

Particle number operator. For the operator $\hat{n}$ the two spinors are eigenstates, $\hat{n}|n\rangle = n|n\rangle$, with $n = 0, 1$. The operator has the following action

$$\hat{n}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = 1\begin{pmatrix} 0 \\ 1 \end{pmatrix}, \tag{3.123}$$
$$\hat{n}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0\begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0, \tag{3.124}$$

and is, therefore, given by a diagonal matrix in this spinor representation with its eigenvalues on the diagonal,[28]

$$\hat{n} \to \langle \alpha|\hat{n}|\beta\rangle = \beta \cdot \hat{1} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}, \tag{3.125}$$

and one readily confirms by direct matrix multiplication that this is consistent with the action of the operator given by Eqs. (3.123) and (3.124).

[28]The first [second] row corresponds to the case $\langle\alpha| = \langle 0|$ [$\langle\alpha| = \langle 1|$], whereas the first [second] column corresponds to $|\beta\rangle = |0\rangle$ [$|\beta\rangle = |1\rangle$].

3.10.3 Spinor representation of $\hat{a}$ and $\hat{a}^\dagger$

Using the definitions (3.61) and (3.62) we readily obtain the matrix elements of the creation and annihilation operators in spinor representation[29]. We again consider the matrices with respect to one of the single-particle states $|\phi_k\rangle$ and take into account that, for fermions, n_k is either 0 or 1. As a result, we obtain

$$\left\langle \alpha_k \left| \hat{a}_k^\dagger \right| \beta_k \right\rangle = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \equiv \mathcal{A}_k^\dagger, \tag{3.126}$$

$$\langle \alpha_k \left| \hat{a}_k \right| \beta_k \rangle = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \equiv \mathcal{A}_k, \tag{3.127}$$

where the matrix of $\hat{a}_k$ is the transposed of that of $\hat{a}_k^\dagger$ and we introduced the short-hand notation $\mathcal{A}_k$ in the space of single-particle orbitals $|\phi_k\rangle$.

We summarize the main properties of the matrices $\mathcal{A}_k$ and $\mathcal{A}_k^\dagger$ which are a consequence of the properties of $\hat{a}_k^\dagger$ and $\hat{a}_k$ and can be verified by direct matrix multiplication:

1. $\mathcal{A}_k^2 = \left(\mathcal{A}_k^\dagger\right)^2 = 0$, which reflects the Pauli principle.
2. $\mathcal{A}_k^\dagger \mathcal{A}_k = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = n_k \hat{1}_k$, – a diagonal matrix with the eigenvalues of $\hat{n}_k$ on the diagonal, cf. Eq. (3.125). This is the spinor representation of $\hat{n}_k$.
3. $\mathcal{A}_k \mathcal{A}_k^\dagger = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = (1 - n_k)\hat{1}_k = \hat{1}_k - \mathcal{A}_k^\dagger \mathcal{A}_k$, i.e. $\mathcal{A}_k^\dagger$ and $\mathcal{A}_k$ anti-commute.
4. For different single-particle spaces, $k \neq l$, $[\mathcal{A}_k^\dagger, \mathcal{A}_l]_+ = [\mathcal{A}_k^\dagger, \mathcal{A}_l^\dagger]_+ = [\mathcal{A}_k, \mathcal{A}_l]_+ = 0$.

3.10.4 Relation to Pauli matrices

The similarity of the basis states and the eigenstates of spin operator $\hat{s}_z$ for spin-1/2 particles, which are both given by two-row spinors, suggests to look for additional similarities on the level of operators. It is easy to see that Pauli matrix σ_z can be reproduced by the following combination of operators,

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \mathcal{A}^\dagger \mathcal{A} - \mathcal{A}\mathcal{A}^\dagger = 2\mathcal{A}^\dagger \mathcal{A} - \hat{1}\,. \tag{3.128}$$

[29] They have the same properties as the spin 1/2 operators $s^\pm$.

Thus, while the fermionic creation and annihilation operators anti-commute, their commutator yields a nontrivial result as well – the Pauli spin matrix σ_z. Obviously, also the spin matrices σ_x and σ_x follow immediately,

$$2\,\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \mathcal{A}^\dagger + \mathcal{A}\,, \tag{3.129}$$

$$2i\,\sigma_y = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = \mathcal{A}^\dagger - \mathcal{A}\,. \tag{3.130}$$

It remains to be verified whether the known properties of the Pauli matrices may be useful for dealing with the second quantization operators.

Problem: Recall the properties of the Pauli spin matrices[30] and apply them to the second quantization operators.

3.10.5 Matrix elements of $\hat{a}$ and $\hat{a}^\dagger$ in Fock space

It is possible to extend the spinor representation to the case of $M > 1$ orbitals. Then, each orbital would be represented by a two-row spinor and operators by $2M \times 2M$ dimensional matrices. However, this quickly becomes inconvenient.

We will, therefore, follow a different route and work with a given set of occupation numbers. These states form an orthonormal system in the anti-symmetric Hilbert space, i.e. $\langle\{n\}|\{n'\}\rangle = \delta_{\{n\},\{n'\}}$. The result is not a matrix any more but a number equal to zero or one. Since the action of the operators $\hat{a}_k$ and $\hat{a}_k^\dagger$ we can immediately compute their matrix elements where the result will be again equal to zero ore one:

$$\boxed{\left\langle \{n\} \left| \hat{a}_k^\dagger \right| \{n'\} \right\rangle = (-1)^{\alpha_k}\, \delta^k_{\{n\},\{n'\}} \delta_{n'_k,0} \delta_{n_k,1}} \tag{3.131}$$

where the original prefactor $1 - n'_k$ has been transformed into an additional Kronecker delta for n_k. The matrix of the annihilation operator is

$$\boxed{\langle \{n\} \left| \hat{a}_k \right| \{n'\} \rangle = (-1)^{\alpha_k}\, \delta^k_{\{n\},\{n'\}}\, \delta_{n'_k,1} \delta_{n_k,0}} \tag{3.132}$$

With these basic results we can easily compute the Fock space matrix elements of arbitrary operators.

[30] See M. Bonitz, "Quantum Mechanics. Lecture Notes"

3.10.6 Matrix elements of one-particle operators in Fock space

To compute the matrix elements of one-particle operators, Eq. (3.44), we need the matrix of the projector $\hat{\Pi}_{kl}$. Using the results (3.132) for the annihiliator and (3.131) for the creator successively we obtain, for the case $k \neq l$,

$$\begin{aligned}
&\left\langle \{n\} \left| \hat{a}_l^\dagger \hat{a}_k \right| \{n'\} \right\rangle = \sum_{\{\bar{n}\}} \left\langle \{n\} \left| \hat{a}_l^\dagger \right| \{\bar{n}\} \right\rangle \langle \{\bar{n}\} \left| \hat{a}_k \right| \{n'\} \rangle = \\
&= (-1)^{\alpha'_k} \sum_{\{\bar{n}\}} (-1)^{\bar{\alpha}_l} \, \delta_{\bar{n}_k,0} \delta^k_{\{\bar{n}\},\{n'\}} \delta_{\bar{n}_k,n'_k-1} \delta_{n_l,1} \delta^l_{\{\bar{n}\},\{n\}} \delta_{\bar{n}_l+1,n_l} \\
&= (-1)^{\alpha'_k} \delta_{n_l,1} \delta^{kl}_{\{n\},\{n'\}} \sum_{\bar{n},\bar{n}_k} (-1)^{\bar{\alpha}_l} \, \delta_{\bar{n}_k,0} \delta_{\bar{n}_k,n_k} \delta_{\bar{n}_l,n'_l} \delta_{\bar{n}_k,n'_k-1} \delta_{\bar{n}_l+1,n_l} \\
&= (-1)^{\alpha_{k'l}} \delta^{kl}_{\{n\},\{n'\}} \delta_{n_l,1} \delta_{n'_l,0} \delta_{n_k,0} \delta_{n'_k,1}, \quad \alpha_{k'l} = \sum_{m<k} n'_m + \sum_{m<l} n_m \,. \qquad (3.133)
\end{aligned}$$

Note that the occupation numbers entering the exponent $\alpha_{k'l}$ are restricted by the Kronecker symbols. For the case $k = l$ we recover the matrix element of the occupation number operator[31]

$$\left\langle \{n\} \left| \hat{a}_k^\dagger \hat{a}_k \right| \{n'\} \right\rangle = \langle \{n\} \left| \hat{n}_k \right| \{n'\} \rangle = n_k \delta_{\{n\},\{n'\}}. \qquad (3.134)$$

Arbitrary single-particle operators. With the results (3.133) and (3.134) we readily obtain the matrix representation of a single-particle operator, defined by Eq. (3.68),

$$\left\langle \{n\} \left| \hat{B}_1 \right| \{n'\} \right\rangle = \sum_{k,l=1}^{\infty} b_{lk} \left\langle \{n\} \left| \hat{a}_l^\dagger \hat{a}_k \right| \{n'\} \right\rangle \qquad (3.135)$$

First, for a diagonal operator B^{diag}, $b_{lk} = b_k \delta_{kl}$, the result is simply

$$\left\langle \{n\} \left| \hat{B}_1^{\mathrm{diag}} \right| \{n'\} \right\rangle = \delta_{\{n\},\{n'\}} \sum_{k=1}^{\infty} b_k n_k = \delta_{\{n\},\{n'\}} \sum_{m=1}^{N} b_{n_m}. \qquad (3.136)$$

where, in the last equality, we have simplified the summation by including only the occupied orbitals (all other orbitals have $n_k = 0$) which have been reordered so that they have the numbers $n_1, n_2 \ldots n_N$.

[31] This result is contained in expression (3.133). Indeed, in the special case $k = l$, we obtain $\alpha_{k'l} \to \sum_{m<k}(n'_m + n_m)$, $\delta^{kl}_{\{n\},\{n'\}} \to \delta^k_{\{n\},\{n'\}}$

For the general case of a non-diagonal operator it follows from (3.135)[32]

$$\left\langle \{n\} \left| \hat{B}_1 \right| \{n'\} \right\rangle = \delta_{\{n\},\{n'\}} \sum_{k=1}^{N} b_{n_k n_k} + \tag{3.137}$$
$$+ \sum_{k\neq l=1}^{N} (-1)^{\alpha_{k'l}+\gamma_{kl}} \, b_{n_l n_k} \, \delta^{n_k n_l}_{\{n\},\{n'\}} \, \delta_{n_l,1}\delta_{n'_l,0}\delta_{n_k,0}\delta_{n'_k,1} \, ,$$

where $\gamma_{kl} = 1$, for $k < l$, and 0, otherwise.

3.10.7 Matrix elements of two-particle operators in Fock space

To compute the matrix elements of two-particle operators, Eq. (3.74), we need the matrix elements of four-operator products, which we transform, using the anti-commutation relations (3.64), according to

$$\hat{a}^\dagger_i \hat{a}^\dagger_j \hat{a}_l \hat{a}_k = -\hat{a}^\dagger_i \hat{a}_l \hat{a}^\dagger_j \hat{a}_k + \delta_{jl} \, \hat{a}^\dagger_i \hat{a}_k. \tag{3.138}$$

Next, transform the matrix element of the first term on the right,

$$\left\langle \{n\} \left| \hat{a}^\dagger_i \hat{a}_l \hat{a}^\dagger_j \hat{a}_k \right| \{n'\} \right\rangle = \sum_{\{\bar{n}\}} \left\langle \{n\} \left| \hat{a}^\dagger_i \hat{a}_l \right| \{\bar{n}\} \right\rangle \left\langle \{\bar{n}\} \left| \hat{a}^\dagger_j \hat{a}_k \right| \{n'\} \right\rangle =$$
$$= \sum_{\{\bar{n}\}} (-1)^{\alpha_{i\bar{l}}} \delta^{il}_{\{n\},\{\bar{n}\}} \delta_{n_i,1}\delta_{\bar{n}_i,0}\delta_{n_l,0}\delta_{\bar{n}_l,1} \times (-1)^{\alpha_{\bar{j}k'}} \delta^{jk}_{\{\bar{n}\},\{n'\}} \delta_{\bar{n}_j,1}\delta_{n'_j,0}\delta_{\bar{n}_k,0}\delta_{n'_k,1},$$

[32] The non-diagonal matrix elements are transformed to summation over occupied orbitals as

$$\sum_{k\neq l=1}^{\infty} b_{lk} \left\langle \{n\} \left| \hat{a}^\dagger_l \hat{a}_k \right| \{n'\} \right\rangle = \sum_{k\neq l=1}^{N} b_{n_l n_k} \left\langle \{n\} \left| \hat{a}^\dagger_{n_l} \hat{a}_{n_k} \right| \{n'\} \right\rangle ,$$

where it remains to carry out the action oft the two operators. Note that the sign of the result is different for $n_l < n_k$ and $n_l > n_k$.

where $\alpha_{\bar{j}k'} = \sum_{p<j} \bar{n}_p + \sum_{p<k} n'_p$ etc. Performing the summation, with the help of the Kronecker deltas we obtain the final result[33]

$$\begin{aligned} \left\langle \{n\} \left| \hat{a}_i^\dagger \hat{a}_l \hat{a}_j^\dagger \hat{a}_k \right| \{n'\} \right\rangle &= (-1)^{\alpha_{ilj'k'}} \delta^{iljk}_{\{n\},\{n'\}} \mathcal{A}_i^\dagger \mathcal{A}_l \mathcal{A}_j^\dagger \mathcal{A}_k \qquad (3.139) \\ \text{with} \quad \alpha_{ilj'k'} &= \sum_{p<i} n_p + \sum_{p<l} n_p + \sum_{p<j} n'_p + \sum_{p<k} n'_p. \end{aligned}$$

This is a general result which also contains the cases of equal index pairs. Then, proceeding as in footnote 31, we obtain the results for the special cases.

i=l: $(-1)^{\alpha_{j'k'}} \delta^{jk}_{\{n\},\{n'\}} n_i \mathcal{A}_j^\dagger \mathcal{A}_k$

j=k: $(-1)^{\alpha_{il}} \delta^{il}_{\{n\},\{n'\}} n_j \mathcal{A}_i^\dagger \mathcal{A}_l$

l=j: $(-1)^{\alpha_{ik'}} \delta^{ik}_{\{n\},\{n'\}} (1 - n_l) \mathcal{A}_i^\dagger \mathcal{A}_k$

i=l, j=k: $\delta_{\{n\},\{n'\}} n_i n_j$

k=i: $(-1)^{\alpha_{lj'}} \delta^{lj}_{\{n\},\{n'\}} n_i \mathcal{A}_l \mathcal{A}_j^\dagger + (-1)^{\alpha_{il}} \delta^{il}_{\{n\},\{n'\}} \delta_{ij} \mathcal{A}_i^\dagger \mathcal{A}_l$

this section is not finished yet!

3.10.8 Fock Matrix of the binary interaction. Slater-Condon rules

Of particular importance is the occupation number matrix representation of the interaction potential. This is an example of a two-particle quantity the properties of which we discussed in section 3.10.7. But for this special case, we can make further progress[34]. Starting point is the pair interaction

$$\hat{W} = \frac{1}{2} \sum_{\alpha \neq \beta = 1}^{N} \hat{w}(\alpha, \beta), \qquad (3.140)$$

[33] We first rewrite

$$\sum_{\{\bar{n}_p\}} \delta^{il}_{\{n\},\{\bar{n}_p\}} \delta^{jk}_{\{\bar{n}_p\},\{n'\}} = \sum_{\bar{n}_i \bar{n}_l \bar{n}_j \bar{n}_k} \delta^{iljk}_{\{n\},\{n'\}} \delta_{n_j,\bar{n}_j} \delta_{n_k,\bar{n}_k} \delta_{\bar{n}_i,n'_i} \delta_{\bar{n}_l,n'_l},$$

Taking into account the other Kronecker deltas we can combine pairs and perform the remaining four summations, $\sum_{\bar{n}_i} \delta_{\bar{n}_i,n'_i} \delta_{\bar{n}_i,0} = \delta_{n'_i,0}$ and so on.

[34] M. Heimsoth contributed to this section.

with the second quantization representation (3.74)

$$\hat{W} = \frac{1}{2}\sum_{ijkl} w_{ijkl}\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k \,. \tag{3.141}$$

The matrix elements are defined as

$$w_{ijkl} = \int d^3x d^3y \, \phi_i^*(\mathbf{x})\phi_j^*(\mathbf{y}) w(\mathbf{x},\mathbf{y})\phi_k(\mathbf{x})\phi_l(\mathbf{y}), \tag{3.142}$$

and have the following symmetries

$$w_{ijkl} = w_{jilk}, \tag{3.143}$$
$$w_{ijkl} = w^*_{klij}, \tag{3.144}$$

where property (3.143) follows from the symmetry of the potential $w(\mathbf{x},\mathbf{y}) = w(\mathbf{y},\mathbf{x})$. This allows us to eliminate double counting of pairs from the sum in Eq. (3.141) by introducing the anti-symmetrized pair potential[35]

$$\hat{W} = \sum_{1\le i<j}^{\infty}\sum_{1\le k<l}^{\infty} w^-_{ijkl}\hat{a}_j^\dagger \hat{a}_i^\dagger \hat{a}_k \hat{a}_l, \tag{3.145}$$
$$w^-_{ijkl} = w_{ijkl} - w_{ijlk} \,. \tag{3.146}$$

Note the change of the order of the creation and annihilation operator pairs in Eq. (3.145).

We now compute the matrix of (3.145) with fully anti-symmetric vectors $|\{n\}\rangle$ and $|\{n'\}\rangle$

$$\langle\{n\}|\hat{W}|\{n'\}\rangle = \sum_{1\le i<j}^{\infty}\sum_{1\le k<l}^{\infty} w^-_{ijkl}\langle\{n\}|\hat{a}_j^\dagger \hat{a}_i^\dagger \hat{a}_k \hat{a}_l|\{n'\}\rangle. \tag{3.147}$$

[35] We summarize the main steps: First, using the anti-commutation relations of the annihilators and performing an index change, we transform (the contribution $k = l$ vanishes),

$$\sum_{kl} w_{ijkl}\hat{a}_l\hat{a}_k = \sum_{k<l}(w_{ijkl} - w_{ijlk})\hat{a}_l\hat{a}_k = \sum_{k<l} w^-_{ijkl}\hat{a}_l\hat{a}_k.$$

Extending this to the sum over i, j and using the symmetry properties (3.143), we obtain

$$\begin{aligned}\sum_{ij,k<l}(w_{ijkl} - w_{ijlk})\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_l\hat{a}_k &= \sum_{i<j,k<l}(w_{ijkl} - w_{jikl} - w_{ijlk} + w_{jilk})\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_l\hat{a}_k = \\ &= 2\sum_{i<j,k<l} w^-_{ijkl}\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_l\hat{a}_k = 2\sum_{i<j,k<l} w^-_{ijkl}\hat{a}_j^\dagger\hat{a}_i^\dagger\hat{a}_k\hat{a}_l\end{aligned}$$

Each of the two vectors contains N particles (the interaction does not change the particle number), i.e. exactly N occupied orbitals, which are all different. So the sums over i, j and k, l, in fact, run over two (possibly different) sets of N orbitals with the numbers $(m_1, m_2 \ldots m_N)$ and $(m'_1, m'_2 \ldots m'_N)$, respectively,[36]

$$\begin{aligned}\langle\{n\}|\hat{W}|\{n'\}\rangle &\rightarrow \langle\{m\}|\hat{W}|\{m'\}\rangle = \\ &= \sum_{1\le i<j}^{N}\sum_{1\le k<l}^{N} w^{-}_{m_i m_j m'_k m'_l}\langle\{m\}|\hat{a}^{\dagger}_{m_j}\hat{a}^{\dagger}_{m_i}\hat{a}_{m'_k}\hat{a}_{m'_l}|\{m'\}\rangle. \quad (3.148)\end{aligned}$$

Using the definitions of the creation and annihilation operators, Eqs. (3.61), (3.62), and taking advantage of the operator order in (3.148)[37], the operators can be evaluated, with the result

$$\begin{aligned}\langle\{m\}|\hat{W}|\{m'\}\rangle = \sum_{1\le i<j}^{N}\sum_{1\le k<l}^{N} (-1)^{i+j+k+l}\, w^{-}_{m_i m_j m'_k m'_l}\langle\{m\}|_{m_i,m_j}|\{m'\}\rangle_{m'_k,m'_l}, \\ \times\, n_{m_j} n_{m_i} n'_{m_k} n'_{m_l} \quad (3.149)\end{aligned}$$

where the notation $|\{m'\}\rangle_{m'_k,m'_l}$ means that the single-particle orbitals with number m'_k and m'_l are missing in the state $|\{m'\}\rangle$ which now is a state of $N-2$ particles, and similarly for $\langle\{m\}|_{m_i,m_j}$. The scalar product of the two anti-symmetric $N-2$-particle states in Eq. (3.149) is non-zero only if the two states contain $N-2$ identical orbitals. To simplify the analysis, in Eq. (3.149) we have moved the missing orbitals to positions one and two in the states thereby accumulating the total sign factor contained in this expression. Thus, the remaining orbitals are not only identical but they also have identical numbers, i.e. $m_3 = m'_3, m_4 = m'_4, \ldots$.

Finally, expression (3.149) will be only non-zero if the missing orbitals fall in one of three cases which will be denoted by I, II and III[38]:

1. The two states are identical, $\{n\} \equiv \{n'\}$ and, consequently $\{m\} \equiv \{m'\}$. Then Eq. (3.149) yields

$$\langle\{n\}|\hat{W}_I|\{n'\}\rangle = \delta_{\{n\},\{n'\}} \sum_{1\le i<j}^{N} w^{-}_{m_i m_j m_i m_j}\, n_{m_i} n_{m_j}\,. \quad (3.150)$$

[36] by $|\{m\}\rangle = |\{m\}\rangle(|\{n\}\rangle)$ we will denote the subset of N occupied orbitals contained in the state $|\{n\}\rangle$. For example, a three-particle state $|\{n\}\rangle = |1,0,0,1,1\rangle$ transforms into $|m_1 m_2 m_3\rangle$ where the m_i point to the original orbitals with numbers $m_1 = 1, m_2 = 4, m_3 = 5$. Note that the matrix $\langle\{n\}|\hat{W}|\{n'\}\rangle$ is diagonal in all orbitals missing simultaneously in $\langle\{m\}|$ and $|\{m'\}\rangle$.

[37] Since $i < j$ and $k < l$, the signs produced by the first and second operators are independent of each other.

[38] Thereby we return to the full vectors (including the empty orbitals) and restore the delta functions.

The specific matrix elements of the interactions that appear in this expression are given by [cf. Eq. (3.142)]

$$w^{-}_{ijij} = \int d^3x\, |\phi_i(\mathbf{x})|^2 \int d^3y\, |\phi_j(\mathbf{y})|^2 w(\mathbf{x},\mathbf{y}) - \\ - \int d^3x\, \phi_i^*(\mathbf{x})\phi_j(\mathbf{x}) \int d^3y\, \phi_j^*(\mathbf{y})\phi_i(\mathbf{y})\, w(\mathbf{x},\mathbf{y})\,. \qquad (3.151)$$

The first integral describes the pair interaction energy of two particles that occupy orbitals ϕ_i and ϕ_j, respectively which extend over the entire space. The y-integral has the meaning of the average interaction potential created by the particle that occupies orbital ϕ_j at space point $\mathbf{x}$, i.e. the induced electrostatic potential $\Phi_i^{\rm ind}(\mathbf{x})$ which is the solution of Poisson's equation. This result is nothing but the Hartree mean field. Similarly, the second integral describes the pair interaction energy of two particles that are not localized in a specific orbital but, instead, make a transition from orbital ϕ_j to orbital ϕ_i and vice versa. This constitutes the exchange contribution to the mean field potential, so the entire expression reproduces the Hartree-Fock mean field. By definition, the remaining two contributions to the potential describe correlation effects.

2. The two states are identical except for one orbital: the orbital m_p with number p is present in state $\langle\{m\}|$ but is missing in state $|\{m'\}\rangle$ which, instead, contains an orbital m_r with number r missing in $\langle\{m\}|$. Then the scalar product of the two $N-2$ particle states is nonzero only if both these states are annihilated and Eq. (3.149) yields[39]

$$\langle\{n\}|\hat{W}_{II}|\{n'\}\rangle = \delta^{m_p m'_r}_{\{n\},\{n'\}} \delta_{n_{m_p},1}\delta_{n'_{m_p},0}\delta_{n_{m_r},0}\delta_{n'_{m_r},1} \times \\ \times \sum_{1\le i, i\ne p,r}^{N-1} (-1)^{p+r}\cdot\Theta(p,r,i)\, w^{-}_{m_i m_p m_i m'_r}\, n_{m_i}\,, \qquad (3.152)$$

where $\Theta(p,r,i) = -1$, if either $m_p < m_i$ or $m'_r < m_i$, otherwise $\Theta(p,r,i) = 1$. The specific matrix elements of the interactions that appear in this expression are given by [cf. Eq. (3.142)]

$$w^{-}_{ipir} = \int d^3y\, \phi_p(\mathbf{y})^* \phi_r(\mathbf{y}) \int d^3x\, |\phi_i(\mathbf{x})|^2 w(\mathbf{x},\mathbf{y}) - \\ - \int d^3x\, \phi_i^*(\mathbf{x})\phi_r(\mathbf{x}) \int d^3y\, \phi_p^*(\mathbf{y})\phi_i(\mathbf{y})\, w(\mathbf{x},\mathbf{y})\,. \qquad (3.153)$$

[39] To obtain the correct sign we move the orbitals p and r to the last place in the product in state $\langle\{n\}|$ and in $|\{n'\}\rangle$, respectively and count the number of transpositions (difference).

This case describes single-particle excitations where $|\{n'\}\rangle = |\{n\}_p^r\rangle$. The first integral describes the coupling of the potential induced by particles in orbital ϕ_i at point $\mathbf{y}$ with a second particle that undergoes a transition from orbital ϕ_r to ϕ_p. The second integral is the exchange correction to the first one. It describes the interaction of a particle pair, one of which makes a transition from orbital ϕ_i to ϕ_p and the other from ϕ_r to ϕ_i.

3. The two states are identical except for two orbitals with the numbers m_p and m_q in $\langle\{m\}|$ and m'_r and m'_s in $|\{m'\}\rangle$, respectively. Without loss of generality we can use $m_p < m_q$ and $m'_r < m'_s$. Then Eq. (3.149) yields

$$\begin{aligned}\langle\{n\}|\hat{W}_{III}|\{n'\}\rangle =& \delta_{\{n\},\{n'\}}^{m_p m_q m'_r m'_s} \delta_{n_{m_p},1}\delta_{n'_{m_p},0}\delta_{n_{m_q},1}\delta_{n'_{m_q},0}\delta_{n_{m_r},0}\delta_{n'_{m_r},1}\delta_{n_{m_s},0}\delta_{n'_{m_s},1} \\ & \times (-1)^{p+q+r+s} w^-_{m_p m_q m'_r m'_s} \,. \end{aligned} \tag{3.154}$$

This case describes two-particle excitations where $|\{n'\}\rangle = |\{n\}_{pq}^{rs}\rangle$.

These results are known as *Slater-Condon rules* and were obtained by those two authors in 1929 and 1930 [Sla29, Con30]. They are of prime importance for wave function based many-body methods, such as configuration interaction (CI) and Multiconfiguration Hartree-Fock (MCHF) and their time-dependent extensions, e.g. [HHB14]. Similarly this representation is used in configuration path integral Monte Carlo simulations of strongly correlated fermions at finite temperature, e.g. [SBF$^+$11] and references therein. This method has been successfully applied to describe the warm dense electron gas [DGB18] and yielded exact results for the thermodynamic properties, e.g. [GDS$^+$17]. The theoretical description of quantum many-particle systems in thermodynamic equilibrium, at a finite temperature, will be discussed in Ch. 4.