Advanced Quantum Mechanics

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Chapter 5

Many-body quantum mechanics

5.1 The many-body space

We consider a quantum system with N *indistinguishable* particles. "Indistingushable" means that those particles exhibit identical properties. That is, they have the same mass, the same spin, they experience the same mutual interaction, and they display the same behaviour in the presence of an external force. N electrons would constitute an example for a set of indistinguishable particles. The concept of indistingushability, however, is not restricted to the realm of elementary particles, but can also arise for composite particles. Hence, also N protons, of which each one consists of two up quarks and one down quark, represent indistinguishable particles, as well as N iron atoms ^{56}Fe, to mention another example, or N oxygene molecules O_2. The "spin" degree of freedom associated with those composite particles comprises then all possible internal excitations of those particles, such as electronic excitations in the case of atoms as well as electronic, vibrational, and rotational excitations in the case of diatomic molecules. Note that the choice of the isotope plays an important role for the notion of indistingushability: A ^{57}Fe atom is clearly distingushable from a ^{56}Fe atom as it exhibits a different mass, a different spin, and one more neutron in its nucleus.

As for any other many-particle or multi-component setting, the quantum state of the system is described by a single complex wavefunction ψ which depends on the individual spatial coordinates $\mathbf{r}_n \in \mathbb{R}^3$ and spins $\sigma_n \in I \subset \frac{1}{2}\mathbb{Z} = \{0, \pm\frac{1}{2}, \pm 1, \pm\frac{3}{2}, \ldots\}$ (*e.g.* $\sigma_n \in \{-\frac{1}{2}, \frac{1}{2}\}$ for electrons) of the particles which we number by the index $n = 1, \ldots, N$. Defining by $\xi_n \equiv (\mathbf{r}_n, \sigma_n)$ the generalized coordinates of particle number n, we can write the wavefunction of the quantum system as

$$\psi \equiv \psi(\xi_1, \ldots, \xi_N) \equiv \psi(\mathbf{r}_1\sigma_1, \ldots, \mathbf{r}_N\sigma_N)\,. \tag{5.1}$$

$|\psi(\xi_1, \ldots, \xi_N)|^2$ then represents the probability density to find particle 1 with spin σ_1 at position $\mathbf{r}_1$, particle 2 with spin σ_2 at position $\mathbf{r}_2$, particle 3 with spin

σ_3 at position $\mathbf{r}_3$, etc. The normalization of the probability density requires that

$$\int d\xi_1 \cdots \int d\xi_N |\psi(\xi_1, \ldots, \xi_N)|^2 \equiv \int d^3 r_1 \sum_{\sigma_1} \cdots \int d^3 r_N \sum_{\sigma_N} |\psi(\mathbf{r}_1 \sigma_1, \ldots, \mathbf{r}_N \sigma_N)|^2 = 1 \tag{5.2}$$

where we define $\int d\xi f(\xi) \equiv \sum_\sigma \int d^3 r f(\mathbf{r}, \sigma)$.

The Hilbert space $\mathcal{H}_1$ associated with one single particle is introduced as the ensemble of all complex functions defined on $\mathbb{R}^3 \times I$ that are square integrable, *i.e.*

$$\mathcal{H}_1 = \left\{ \psi : \mathbb{R}^3 \times I \to \mathbb{C}, \xi \equiv (\mathbf{r}, \sigma) \mapsto \psi(\xi) \equiv \psi(\mathbf{r}, \sigma) \text{ with } \int d\xi |\psi(\xi)|^2 < \infty \right\}. \tag{5.3}$$

Within $\mathcal{H}_1$ we can introduce an orthonormal basis

$$\mathcal{B}_1 = (|\phi_0\rangle, |\phi_1\rangle, \ldots) \equiv (|\phi_k\rangle)_{k \in \mathbb{N}_0} \tag{5.4}$$

consisting of wavefunctions $\phi_k \in \mathcal{H}_1$ that satisfy the orthogonality relations

$$\langle \phi_k | \phi_{k'} \rangle = \int d\xi \langle \phi_k | \xi \rangle \langle \xi | \phi_{k'} \rangle = \int d\xi \phi_k^*(\xi) \phi_{k'}(\xi) = \delta_{kk'} \tag{5.5}$$

for all $k, k' \in \mathbb{N}_0$, where we identify $\langle \xi | \phi \rangle \equiv \phi(\xi)$. These basis states can be used to represent operators $A : \mathcal{H}_1 \to \mathcal{H}_1$ which correspond to linear transformations $\psi \mapsto A\psi$ within $\mathcal{H}_1$. We can write

$$A = \sum_{k,k'=0}^{\infty} A_{kk'} |\phi_k\rangle\langle\phi_{k'}| \qquad \text{with} \quad A_{kk'} = \langle \phi_k | A | \phi_{k'} \rangle . \tag{5.6}$$

The Hilbert space describing N such particles is then given by the direct product of N Hilbert spaces $\mathcal{H}_1$ and reads

$$\begin{aligned} \mathcal{H}_N &= \underbrace{\mathcal{H}_1 \times \ldots \times \mathcal{H}_1}_{N \text{ times}} \\ &= \{\psi : (\mathbb{R}^3 \times I) \times \ldots \times (\mathbb{R}^3 \times I) \to \mathbb{C}, (\xi_1, \ldots, \xi_N) \mapsto \psi(\xi_1, \ldots, \xi_N) \\ &\quad \text{with} \int d\xi_1 \cdots \int d\xi_N |\psi(\xi_1, \ldots, \xi_N)|^2 < \infty \} . \end{aligned} \tag{5.7}$$

Using the elements $|\phi_k\rangle$ of $\mathcal{B}_1$, we can construct an orthonormal basis $\mathcal{B}_N$ of $\mathcal{H}_N$ through

$$\mathcal{B}_N = (|\phi_{k_1} \phi_{k_2} \cdots \phi_{k_N}\rangle)_{k_1, \ldots, k_N \in \mathbb{N}_0} \tag{5.8}$$

where we define

$$|\phi_{k_1} \phi_{k_2} \cdots \phi_{k_N}\rangle \equiv |\phi_{k_1}\rangle |\phi_{k_2}\rangle \cdots |\phi_{k_N}\rangle \quad \text{and} \tag{5.9}$$

$$\langle \phi_{k_1} \phi_{k_2} \cdots \phi_{k_N}| \equiv \langle \phi_{k_N}| \cdots \langle \phi_{k_2}| \langle \phi_{k_1}| . \tag{5.10}$$

The orthogonality relations of those many-body basis states read

$$\begin{aligned}\langle\phi_{k'_1}\cdots\phi_{k'_N}|\phi_{k_1}\cdots\phi_{k_N}\rangle &= \left(\langle\phi_{k'_N}|\cdots\langle\phi_{k'_1}|\right)\left(|\phi_{k_1}\rangle\cdots|\phi_{k_N}\rangle\right)\\ &= \langle\phi_{k'_1}|\phi_{k_1}\rangle\cdots\langle\phi_{k'_N}|\phi_{k_N}\rangle\\ &= \delta_{k_1k'_1}\cdots\delta_{k_Nk'_N}\end{aligned} \tag{5.11}$$

while the associated wavefunctions in the many-body coordinate space can be expressed as

$$\langle\xi_1,\ldots,\xi_N|\phi_1,\ldots,\phi_N\rangle = \phi_1(\xi_1)\cdots\phi_N(\xi_N)\,. \tag{5.12}$$

The concept of one-body operators can also be generalized for the many-particle Hilbert space. In the case of indistinguishable particles, it makes sense to introduce the *total operator* $\hat{A}:\mathcal{H}_N\to\mathcal{H}_N$ that is associated with a given single-particle operator A[1]. The transformation $\psi\mapsto\hat{A}\psi$ consists in summing up the applications of A to each individual particle of the system. More quantitatively, the basis state $|\phi_{k_1}\phi_{k_2}\cdots\phi_{k_N}\rangle\equiv|\phi_{k_1}\rangle|\phi_{k_2}\rangle\cdots|\phi_{k_N}\rangle$ is transformed under $\hat{A}$ according to

$$\begin{aligned}\hat{A}|\phi_{k_1}\rangle|\phi_{k_2}\rangle|\phi_{k_3}\rangle\cdots|\phi_{k_{N-1}}\rangle|\phi_{k_N}\rangle &= |A\phi_{k_1}\rangle|\phi_{k_2}\rangle|\phi_{k_3}\rangle\cdots|\phi_{k_{N-1}}\rangle|\phi_{k_N}\rangle\\ &+ |\phi_{k_1}\rangle|A\phi_{k_2}\rangle|\phi_{k_3}\rangle\cdots|\phi_{k_{N-1}}\rangle|\phi_{k_N}\rangle\\ &+ \ldots\\ &+ |\phi_{k_1}\rangle|\phi_{k_2}\rangle|\phi_{k_3}\rangle\cdots|\phi_{k_{N-1}}\rangle|A\phi_{k_N}\rangle\end{aligned} \tag{5.13}$$

Using the representation (5.6) of A in the single-particle basis $\mathcal{B}_1$, we can write

$$\hat{A}=\sum_{k_1=0}^{\infty}\cdots\sum_{k_N=0}^{\infty}\sum_{n=1}^{N}\sum_{k'_n=0}^{\infty}A_{k_nk'_n}|\phi_{k_1}\cdots\phi_{k_{n-1}}\phi_{k_n}\phi_{k_{n+1}}\cdots\phi_{k_N}\rangle\langle\phi_{k_1}\cdots\phi_{k_{n-1}}\phi_{k'_n}\phi_{k_{n+1}}\cdots\phi_{k_N}|\,. \tag{5.14}$$

Let us consider as an example the kinetic energy of a quantum particle with mass m. The associated one-body operator reads

$$T=\frac{\mathbf{p}^2}{2m}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}^2}\,. \tag{5.15}$$

According to the above prescription, the associated total operator in the Hilbert space of N such particles is then simply given by the familiar expression for the total kinetic energy

$$\hat{T}=-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial\mathbf{r}_1^2}+\ldots+\frac{\partial^2}{\partial\mathbf{r}_N^2}\right) \tag{5.16}$$

of all particles. Indeed, this total kinetic energy (or equivalently, the average kinetic energy per particle, corresponding to the operator $\hat{T}/N$) represents a

[1]Hats will, in the following, exclusively be used for operators that are defined within the many-body space $\mathcal{H}_N$.

measurable observable in a system of N identical particles, while the individual kinetic energy of, say, particle number 3 has no physical meaning as it is practically impossible in an experiment to tag individual number labels to those particles. This latter consideration leads to the statement that those particles are essentially *identical*.

5.2 The symmetry postulate

In view of this latter observation, we can now formulate the symmetry postulate for a system of indistinguishable quantum particles. Colloquially speaking, it implies that all those particles have to be treated in an identical manner, not only from the point of view of physical observables, but also on the level of the wavefunction of the system.

To this end, we start by noting that a system of N indistinguishable particles is characterized by possessing a Hamiltonian that is invariant under permutations of individual particles. As an example, let us consider a system of N particles with mass m that are subject to the external potential $V(\mathbf{r})$ and interact with each other via the two-body interaction potential $U(\mathbf{r},\mathbf{r}') \equiv U(\mathbf{r}-\mathbf{r}')$ which depends only on the distance $|\mathbf{r}-\mathbf{r}'|$ between the particles. The corresponding many-body Hamiltonian reads

$$\hat{H} \equiv \hat{H}(\mathbf{p}_1,\mathbf{r}_1,\ldots,\mathbf{p}_N,\mathbf{r}_N) = \sum_{n=1}^{N}\left(\frac{\mathbf{p}_n^2}{2m}+V(\mathbf{r}_n)\right)+\frac{1}{2}\sum_{n\neq n'=1}^{N}U(\mathbf{r}_n-\mathbf{r}_{n'})\,. \quad (5.17)$$

Clearly, $\hat{H}$ is invariant with respect to any permutation of the particles. We have for instance $\hat{H}(\mathbf{p}_1,\mathbf{r}_1,\mathbf{p}_2,\mathbf{r}_2,\ldots,\mathbf{p}_N,\mathbf{r}_N) = \hat{H}(\mathbf{p}_N,\mathbf{r}_N,\ldots,\mathbf{p}_2,\mathbf{r}_2,\mathbf{p}_1,\mathbf{r}_1)$.

On a more formal level, $\hat{H}$ commutes with any operator $\hat{\Pi}_{nn'}$ that exchanges two particles in the wavefunction. We name $\hat{\Pi}_{nn'}$ *transposition operator* in the following, and it is defined through

$$\left(\hat{\Pi}_{nn'}\psi\right)(\xi_1,\ldots,\xi_n,\ldots,\xi_{n'},\ldots,\xi_N) = \psi(\xi_1,\ldots,\xi_{n'},\ldots,\xi_n,\ldots,\xi_N) \quad (5.18)$$

for $n,n' = 1,\ldots,N$. Obviously we have $\hat{\Pi}_{nn'} = \hat{\Pi}_{n'n} = \hat{\Pi}_{nn'}^\dagger$ and $\hat{\Pi}_{nn'}^2 = \mathbb{I}$. This means that $\hat{\Pi}_{nn'}$ is both hermitian and unitary, and its eigenvalues are ± 1. The associated eigenfunctions satisfy

$$\psi(\xi_1,\ldots,\xi_n,\ldots,\xi_{n'},\ldots,\xi_N) = \pm\psi(\xi_1,\ldots,\xi_{n'},\ldots,\xi_n,\ldots,\xi_N)\,, \quad (5.19)$$

i.e., they are symmetric (for the eigenvalue $+1$) or antisymmetric (for the eigenvalue -1) with respect to the exchange of the coordinates ξ_n and $\xi_{n'}$.

Since $[\hat{H},\hat{\Pi}_{nn'}] = 0$ for all $n,n' = 1,\ldots,N$, it is natural to speculate about choosing a common eigenbasis of all $\hat{\Pi}_{nn'}$ in which the many-body Hamiltonian

is to be diagonalized. In general, however, the transposition operators do not commute with each other. This can be explicitly worked out for the specific case of the operators $\hat{\Pi}_{12}$ and $\hat{\Pi}_{23}$. We have

$$\left(\hat{\Pi}_{12}\hat{\Pi}_{23}\psi\right)(\xi_1,\xi_2,\xi_3,\ldots) = \left(\hat{\Pi}_{23}\psi\right)(\xi_2,\xi_1,\xi_3,\ldots) = \psi(\xi_2,\xi_3,\xi_1,\ldots) \tag{5.20}$$

and

$$\left(\hat{\Pi}_{23}\hat{\Pi}_{12}\psi\right)(\xi_1,\xi_2,\xi_3,\ldots) = \left(\hat{\Pi}_{12}\psi\right)(\xi_1,\xi_3,\xi_2,\ldots) = \psi(\xi_3,\xi_1,\xi_2,\ldots) \tag{5.21}$$

for any wavefunction $\psi \in \mathcal{H}_N$. Hence, in order for $\hat{\Pi}_{12}\hat{\Pi}_{23}\psi = \hat{\Pi}_{23}\hat{\Pi}_{12}\psi$ to hold (and in order for $\hat{\Pi}_{12}\hat{\Pi}_{13}\psi = \hat{\Pi}_{13}\hat{\Pi}_{12}\psi$ and $\hat{\Pi}_{13}\hat{\Pi}_{23}\psi = \hat{\Pi}_{23}\hat{\Pi}_{13}\psi$ to hold as well) we need to require that ψ is either *entirely symmetric* or *entirely antisymmetric* in its first three coordinates ξ_1, ξ_2, ξ_3. That is, ψ has to be common eigenfunction of all $\hat{\Pi}_{nn'}$ with $n, n' = 1, 2, 3$, with eigenvalues that can be either $+1$ for all $\hat{\Pi}_{nn'}$ or -1 for all $\hat{\Pi}_{nn'}$. A "mixed" choice for the eigenvalues of ψ, *e.g.* $\hat{\Pi}_{12}\psi = \psi$ and $\hat{\Pi}_{23}\psi = -\psi$, is not possible and would lead to a contradiction, since in that case it would not be possible to specify how the operator $\hat{\Pi}_{13} = \hat{\Pi}_{12}\hat{\Pi}_{23}\hat{\Pi}_{12} = \hat{\Pi}_{23}\hat{\Pi}_{12}\hat{\Pi}_{23}$ acts on ψ.

This reasoning can be generalized for the other transposition operators as well. We thereby arrive at the conclusion that the transposition operators $\hat{\Pi}_{nn'}$ commute with each other only within the two orthogonal subspaces

$$\mathcal{H}_N^{\pm} = \left\{\psi \in \mathcal{H}_N : \hat{\Pi}_{nn'}\psi = \pm\psi \text{ for all } n, n' = 1, \ldots, N\right\} \tag{5.22}$$

of the Hilbert space $\mathcal{H}_N$, which contain those wavefunctions ψ that are entirely symmetric ($\mathcal{H}_N^+$) or entirely antisymmetric ($\mathcal{H}_N^-$) with respect to the exchange of two particles. As a consequence, since $[\hat{H}, \hat{\Pi}_{nn'}] = 0$ for all $n, n' = 1, \ldots, N$, the Hamiltonian $\hat{H}$ as well as the time evolution operator $\exp(-it\hat{H}/\hbar)$ (or $\mathcal{T}\exp[-i\int_0^t \hat{H}(t')dt'/\hbar]$ for explicitly time-dependent Hamiltonians $\hat{H} \equiv \hat{H}(t)$, with $\mathcal{T}$ the time-ordering operator) represent *endomorphisms* within the subspaces $\mathcal{H}_N^{\pm}$, *i.e.* they map an element of $\mathcal{H}_N^{\pm}$ to another element of $\mathcal{H}_N^{\pm}$. Hence, a many-body wavefunction that is initially entirely symmetric (or entirely antisymmetric) with respect to the exchange of particles will keep this particular property in the course of the time evolution generated by the Hamiltonian $\hat{H}$.

The symmetry postulate can now be formulated by stating that physically relevant quantum states describing a system of N identical particles are *either elements of* $\mathcal{H}_N^+$ *or elements of* $\mathcal{H}_N^-$. That is, the wavefunction of such a system is either *entirely symmetric* or *entirely antisymmetric* with respect to the exchange of the spatial coordinates and spins within any pair of two particles. In the former, symmetric case, those particles are named *bosons* or *bosonic particles*, while in the latter, antisymmetric case we are talking about *fermions* or *fermionic particles*. Obviously, physically relevant observables must correspond to *total operators* which commute with all transposition operators $\hat{\Pi}_{nn'}$ for $n, n' = 1, \ldots, N$.

Indeed, it must not be possible to break the symmetry or antisymmetry of the wavefunction by the projection process that happens in the course of a quantum measurement associated with such an observable.

5.3 Construction of a symmetric or antisymmetric basis

Having defined the symmetric and antisymmetric subspaces $\mathcal{H}_N^\pm$ of the N-particle Hilbert space $\mathcal{H}_N$, we now address the problem of constructing an orthonormal basis $\mathcal{B}_N^\pm$ within $\mathcal{H}_N^\pm$ using the one-body states $|\phi_k\rangle$ of the basis (5.4) within the single-particle Hilbert space $\mathcal{H}_1$. It seems obvious that one should take for this purpose the many-particle basis states $|\phi_{k_1}\cdots\phi_{k_N}\rangle \in \mathcal{B}_N$, defined in Eqs. (5.9) and (5.10), and symmetrize or antisymmetrize them properly. It is less obvious, however, how to avoid multiple counting of identical basis states in the course of this procedure, and how to correctly normalize the resulting basis states.

Let us first consider the relatively easy case of $N = 2$ particles. The two-particle Hilbert space $\mathcal{H}_2$ is spanned by the basis $\mathcal{B}_2 = (|\phi_{k_1}\phi_{k_2}\rangle)_{k_1,k_2\in\mathbb{N}_0}$ with $|\phi_{k_1}\phi_{k_2}\rangle \equiv |\phi_{k_1}\rangle|\phi_{k_2}\rangle$. Symmetrizing and antisymmetrizing yields the basis states

$$|\phi^\pm_{k_1k_2}\rangle = \mathcal{A}^\pm_{k_1k_2}\left(|\phi_{k_1}\phi_{k_2}\rangle \pm |\phi_{k_2}\phi_{k_1}\rangle\right) \tag{5.23}$$

for the symmetric and antisymmetric subspaces $\mathcal{H}_2^\pm$, respectively. While the orthogonality between different basis states $|\phi^\pm_{k_1k_2}\rangle$ is granted, double counting of identical states (or, more generally, of states that are identical up to a global sign) has to be avoided, *e.g.*, by imposing that k_2 must not be larger than k_1. We therefore require $k_2 \leq k_1$ for the definition of $|\phi^+_{k_1k_2}\rangle$ as well as $k_2 < k_1$ for the definition of $|\phi^-_{k_1k_2}\rangle$. Indeed, the case $k_1 = k_2$ does not make any sense for the basis functions of $\mathcal{H}_2^-$ as one would have $|\phi^-_{k_1k_1}\rangle = 0$ from Eq. (5.23). In other words, two fermionic particles cannot share the same single-particle state $|\phi_{k_1}\rangle$.

With this additional requirement, and using the orthogonality and normalization of the single-particle states $|\phi_k\rangle$, we obtain

$$\langle\phi^+_{k_1k_2}|\phi^+_{k_1'k_2'}\rangle = 2(\mathcal{A}^+_{k_1k_2})^*\mathcal{A}^+_{k_1'k_2'}\delta_{k_1k_1'}\delta_{k_2k_2'}(1+\delta_{k_1k_2})\,, \tag{5.24}$$

$$\langle\phi^-_{k_1k_2}|\phi^-_{k_1'k_2'}\rangle = 2(\mathcal{A}^-_{k_1k_2})^*\mathcal{A}^-_{k_1'k_2'}\delta_{k_1k_1'}\delta_{k_2k_2'}\,. \tag{5.25}$$

The normalization condition $\langle\phi^\pm_{k_1k_2}|\phi^\pm_{k_1'k_2'}\rangle = \delta_{k_1k_1'}\delta_{k_2k_2'}$ then leads to the choice $\mathcal{A}^\pm_{k_1k_2} = 1/\sqrt{2}$ for $k_1 > k_2$ as well as $\mathcal{A}^+_{k_1k_1} = 1/2$ in the special case of bosons. We therefore obtain the orthogonal and normalized basis states

$$|\phi^\pm_{k_1k_2}\rangle = \frac{1}{\sqrt{2}}\left(|\phi_{k_1}\phi_{k_2}\rangle \pm |\phi_{k_2}\phi_{k_1}\rangle\right) \tag{5.26}$$

for $k_1, k_2 \in \mathbb{N}_0$ with $k_1 > k_2$ as well as

$$|\phi^+_{kk}\rangle = |\phi_k \phi_k\rangle \tag{5.27}$$

for $k \in \mathbb{N}_0$ in the case of bosons.

The case of $N = 3$ particles can be treated in perfect analogy. We obtain

$$\begin{aligned} |\phi^\pm_{k_1 k_2 k_3}\rangle &= \frac{1}{\sqrt{6}}(|\phi_{k_1}\phi_{k_2}\phi_{k_3}\rangle + |\phi_{k_2}\phi_{k_3}\phi_{k_1}\rangle + |\phi_{k_3}\phi_{k_1}\phi_{k_2}\rangle \\ &\quad \pm|\phi_{k_2}\phi_{k_1}\phi_{k_3}\rangle \pm |\phi_{k_3}\phi_{k_2}\phi_{k_1}\rangle \pm |\phi_{k_1}\phi_{k_3}\phi_{k_2}\rangle) \end{aligned} \tag{5.28}$$

as basis states within $\mathcal{H}^\pm_3$ for $k_1, k_2, k_3 \in \mathbb{N}_0$ with $k_1 > k_2 > k_3$. For the special case of bosons, we have, in addition, also the basis states

$$|\phi^+_{k_1 k_1 k_2}\rangle = \frac{1}{\sqrt{3}}(|\phi_{k_1}\phi_{k_1}\phi_{k_2}\rangle + |\phi_{k_1}\phi_{k_2}\phi_{k_1}\rangle + |\phi_{k_2}\phi_{k_1}\phi_{k_1}\rangle)\,, \tag{5.29}$$

$$|\phi^+_{k_1 k_2 k_2}\rangle = \frac{1}{\sqrt{3}}(|\phi_{k_1}\phi_{k_2}\phi_{k_2}\rangle + |\phi_{k_2}\phi_{k_1}\phi_{k_2}\rangle + |\phi_{k_2}\phi_{k_2}\phi_{k_1}\rangle) \tag{5.30}$$

for $k_1, k_2 \in \mathbb{N}_0$ with $k_1 > k_2$ as well as

$$|\phi^+_{kkk}\rangle = |\phi_k \phi_k \phi_k\rangle \tag{5.31}$$

for $k \in \mathbb{N}_0$.

In order to generalize for the case of $N > 3$ particles, we need to introduce the concept of *permutations*. In most general terms, a permutation is an invertible transformation that maps elements of a finite set onto each other. For the specific case of the set of integers $\{1, \ldots, N\}$, we can define the set of permutations that act upon $\{1, \ldots, N\}$ as

$$\begin{aligned} \Pi_N &= \{\pi : \{1, \ldots, N\} \to \{1, \ldots, N\}, n \mapsto \pi(n) \text{ with the property:} \\ &\quad \pi(n) = \pi(n') \text{ if and only if } n = n' \text{ for all } n, n' = 1, \ldots, N\}\,. \end{aligned} \tag{5.32}$$

Clearly, Π_N represents a group since the combination $\pi \circ \pi'$ of two permutations $\pi, \pi' \in \Pi_N$, defined through $(\pi \circ \pi')(n) = \pi(\pi'(n))$ for all $n \in \{1, \ldots, N\}$, is also an element of Π_N. By definition, there exists an inverse permutation $\pi^{-1} \in \Pi_N$ to each $\pi \in \Pi_N$ such that $\pi^{-1} \circ \pi$ is the identity element of Π_N that maps each number $n \in \{1, \ldots, N\}$ onto itself.

One can show that Π_N consists of $N!$ different elements, *i.e.*, there are $N!$ different possibilities to permute the numbers $1, \ldots, N$. One can furthermore show that each permutation $\pi \in \Pi_N$ can be represented as a sequence of individual *transpositions* $\pi_{ij} \in \Pi_N$ that exchange two numbers $i, j \in \{1, \ldots, N\}$ and map the other numbers within $\{1, \ldots, N\}$ onto themselves. We can therefore write

$$\pi = \pi_{i_1 j_1} \circ \pi_{i_2 j_2} \circ \ldots \circ \pi_{i_M j_M} \tag{5.33}$$

using a sequence of transpositions $\pi_{i_m j_m} \in \Pi_N$ with $m = 1, \ldots, M$. Note that neither the choice of the transpositions $\pi_{i_m j_m}$ that are used to represent π nor even their number M are uniquely defined for a given permutation $\pi \in \Pi_N$. Indeed, the permutation π that exchanges the numbers 1 and 3 while mapping the other numbers onto themselves can obviously be expressed as $\pi = \pi_{13}$, but also, as was already mentioned in the previous section 5.2, as $\pi = \pi_{12}\pi_{23}\pi_{12}$ or $\pi = \pi_{23}\pi_{12}\pi_{23}$ or $\pi = \pi_{12}\pi_{23}\pi_{12}\pi_{13}\pi_{13}$, to mention some examples.

Note, however, that it is not possible to represent the above permutation π_{13} by an *even* number of transpositions. On a more general level, a remarkable property of permutations is that the number M of transpositions used in a representation (5.33) of a given permutation $\pi \in \Pi_N$ is either even for all possible representations, in which case π is said to be an *even* permutation, or odd for all possible representations, in which case π is said to be an *odd* permutation. We can therefore associate with each permutation $\pi \in \Pi_N$ a well-defined parity which is independent of its specific representation in terms of transpositions, and which can be expressed through the introduction of the *sign* or *signature*

$$(-1)^\pi \equiv \prod_{n=2}^{N} \prod_{n'=1}^{n-1} \frac{\pi(n) - \pi(n')}{n - n'} = (-1)^M = \begin{cases} +1 : \pi \text{ is an even permutation} \\ -1 : \pi \text{ is an odd permutation} \end{cases} \tag{5.34}$$

of the permutation π.

We are now in a position to express the entirely symmetric and antisymmetric basis states $|\phi^\pm_{k_1 \ldots k_N}\rangle$ within $\mathcal{H}^\pm_N$ in terms of sums over permutations of the quantum numbers $k_1, \ldots, k_N$. Defining by convention $(+1)^\pi \equiv 1$ for each $\pi \in \Pi_N$, we write

$$|\phi^\pm_{k_1 \cdots k_N}\rangle = \mathcal{A}^\pm_{k_1 \cdots k_N} \sum_{\pi \in \Pi_N} (\pm 1)^\pi |\phi_{k_{\pi(1)}} \cdots \phi_{k_{\pi(N)}}\rangle \tag{5.35}$$

for bosons $(+)$ and fermions $(-)$. The associated wavefunction reads

$$\langle \xi_1 \cdots \xi_N | \phi^\pm_{k_1 \cdots k_N}\rangle = \mathcal{A}^\pm_{k_1 \cdots k_N} \sum_{\pi \in \Pi_N} (\pm 1)^\pi \phi_{k_{\pi(1)}}(\xi_1) \cdots \phi_{k_{\pi(N)}}(\xi_N)\,. \tag{5.36}$$

To avoid double counting, we require $k_1 \geq k_2 \geq \ldots \geq k_N$ for bosons as well as $k_1 > k_2 > \ldots > k_N$ for fermions. The normalization condition

$$\langle \phi^\pm_{k_1 \cdots k_N} | \phi^\pm_{k'_1 \cdots k'_N}\rangle = \delta_{k_1 k'_1} \cdots \delta_{k_N k'_N} \tag{5.37}$$

is then satisfied in the case of fermions if we choose $\mathcal{A}^-_{k_1 \cdots k_N} = 1/\sqrt{N!}$ for all $k_1, \ldots, k_N \in \mathbb{N}_0$. We can then express the fermionic many-body wavefunction in terms of the determinant of a $N \times N$ complex matrix, namely through

$$\langle \xi_1 \cdots \xi_N | \phi^-_{k_1 \cdots k_N}\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{k_1}(\xi_1) & \cdots & \phi_{k_N}(\xi_1) \\ \vdots & & \vdots \\ \phi_{k_1}(\xi_N) & \cdots & \phi_{k_N}(\xi_N) \end{vmatrix}, \tag{5.38}$$

which is also named *Slater determinant*.

In the case of bosons, we have to account for possible multiple appearances of a given single-particle state $|\phi_k\rangle$ within $|\phi_{k_1}\cdots\phi_{k_N}\rangle$. To this end, we define by $n_k \in \{0,1,\ldots,N\}$ the number of times that the integer k appears within the set $\{k_1,\ldots,k_N\}$. We can then choose

$$\mathcal{A}^+_{k_1\cdots k_N} = \frac{1}{\sqrt{N!\prod_{k=0}^{\infty} n_k!}} = \frac{1}{\sqrt{N! n_0! n_1! n_2!\cdots}} \tag{5.39}$$

in order to satisfy the normalization condition (5.37). As $0! = 1! = 1$, we would recover the same choice as for fermions, $\mathcal{A}^+_{k_1\cdots k_N} = 1/\sqrt{N!}$, in the special case $k_1 > k_2 > \ldots > k_N$, while for the opposite case $k_1 = k_2 = \ldots = k_N$ we would have $n_{k_1} = N$ and thereby $\mathcal{A}^+_{k_1\cdots k_N} = 1/N!$, which correctly accounts for the fact that $N!$ identical terms $|\phi_{k_1}\cdots\phi_{k_1}\rangle$ would, in that case, be summed in the expression (5.35).

Observing that in the case of fermions we would have $n_k = 0$ or 1 and hence $n_k! = 1$ for all $k \in \mathbb{N}_0$, we can finally express the correctly normalized basis states within $\mathcal{H}_N^{\pm}$ as

$$|\phi^{\pm}_{k_1\cdots k_N}\rangle = \frac{1}{\sqrt{N!\prod_{k=0}^{\infty} n_k!}} \sum_{\pi\in\Pi_N} (\pm 1)^{\pi} |\phi_{k_{\pi(1)}}\cdots\phi_{k_{\pi(N)}}\rangle \tag{5.40}$$

for bosons as well as for fermions. An immediate consequence of this form of the basis states in the case of fermions is the *Pauli exclusion principle* which states that it is impossible for two or more identical fermions to occupy the same single-particle state $|\phi\rangle$ or to be measured with the same generalized coordinates $\xi \equiv (\mathbf{r},\sigma)$, *i.e.*, with the same spin σ at the same place $\mathbf{r}$. Indeed, the Slater determinant (5.38) would, in those two cases, obviously be identical to zero.

Let us finally address the question how to represent physically relevant operators within this symmetrized or antisymmetrized basis. As was already stated in Eq. (5.6), one-body operators $A : \mathcal{H}_1 \to \mathcal{H}_1$ are represented within the single-particle basis $\mathcal{B}_1 = (|\phi_k\rangle)_{k\in\mathbb{N}_0}$ according to

$$A = \sum_{k,k'=0}^{\infty} A_{kk'} P_{kk'} \tag{5.41}$$

with $A_{kk'} = \langle\phi_k|A|\phi_{k'}\rangle$ where we define the (in general non-hermitian) one-body operator

$$P_{kk'} = |\phi_k\rangle\langle\phi_{k'}| \,. \tag{5.42}$$

The associated total operator in the many-body space can then be written as

$$\hat{A} = \sum_{k,k'=0}^{\infty} A_{kk'} \hat{P}_{kk'} \tag{5.43}$$

where $\hat{P}_{kk'}$ represents the many-body equivalent of $P_{kk'}$. In analogy with Eq. (5.14) we obtain

$$\hat{P}_{kk'}|\phi_{k_1}\cdots\phi_{k_N}\rangle = \sum_{n=1}^{N}\delta_{k'k_n}|\phi_{k_1}\cdots\phi_{k_{n-1}}\phi_k\phi_{k_{n+1}}\cdots\phi_{k_N}\rangle \tag{5.44}$$

and hence

$$\hat{P}_{kk'}|\phi^{\pm}_{k_1\cdots k_N}\rangle = \frac{1}{\sqrt{N!\prod_{k=0}^{\infty}n_k!}}\sum_{\pi\in\Pi_N}(\pm 1)^{\pi}\sum_{n=1}^{N}\delta_{k'k_{\pi(n)}}|\phi_{k_{\pi(1)}}\cdots\phi_{k_{\pi(n-1)}}\phi_k\phi_{k_{\pi(n+1)}}\cdots\phi_{k_{\pi(N)}}\rangle\,. \tag{5.45}$$

Therefore, $\hat{P}_{kk'}|\phi^{\pm}_{k_1\cdots k_N}\rangle = 0$ if $k'\notin\{k_1,\ldots,k_N\}$, while otherwise, if $k'=k_n$ for a $n\in\{1,\ldots,N\}$, we have

$$\hat{P}_{kk'}|\phi^{\pm}_{k_1\cdots k_N}\rangle = \alpha^{\pm}_{kk'}|\phi^{\pm}_{k_1\cdots k_{n-1}k_{n+1}\cdots k_\nu k k_{\nu+1}\cdots k_N}\rangle \tag{5.46}$$

for some prefactor $\alpha^{\pm}_{kk'}$, where the index ν is determined such that $k_\nu\geq k\geq k_{\nu+1}$[2].

In the case of bosons, the precise ordering of the quantum numbers is, in practice, not relevant as the basis states of the bosonic subspace are entirely symmetric. However, we do have to take into account the possibility of multiple appearances of the quantum number k' within $\{k_1,\ldots,k_N\}$, which would give rise to multiple, namely $n_{k'}$, possibilities of replacing $\phi_{k'}$ by ϕ_k in the sum over n on the right-hand side of Eq. (5.45). $n_{k'}$ is consequently decremented by 1 after this replacement, and n_k is incremented by 1, which in turn gives rise to different normalization prefactors of the basis state. We therefore have to choose the prefactor in Eq. (5.46) as

$$\alpha^{+}_{kk'} = n_{k'}\sqrt{\frac{(n_{k'}-1)!}{n_{k'}!}}\sqrt{\frac{(n_k+1)!}{n_k!}} = \sqrt{n_{k'}(n_k+1)}\,. \tag{5.47}$$

In the fermionic case, the normalization prefactor $1/\sqrt{N!}$ of the basis state is not affected by the replacement of $\phi_{k'}$ by ϕ_k. However, we have pay attention to the fact that $\hat{P}_{kk'}|\phi^{\pm}_{k_1\cdots k_N}\rangle = 0$ if $k=k_\nu\neq k'$ for a $\nu\in\{1,\ldots,N\}$, due to the Pauli principle. Moreover, we have to take into account that the necessary re-ordering of the quantum numbers $k_1>\ldots>k_N$ after the replacement of k' by k might involve a sign change, corresponding to the sign of the permutation that performs this re-ordering, when we want to express the right-hand side of Eq. (5.45) in terms of the (properly ordered) many-body basis state $|\phi^{\pm}_{k_1\cdots k\cdots k_N}\rangle$. To account for this sign change as well as for the Pauli principle, we choose the prefactor in Eq. (5.46) as

$$\alpha^{-}_{kk'} = n_{k'}(1-n_k)(-1)^{n_0+n_1+\ldots+n_{k'-1}}(-1)^{n_0+n_1+\ldots+n_{k-1}} = n_{k'}(1-n_k)(-1)^{\mathcal{N}} \tag{5.48}$$

[2]Obviously, in the presentation of Eq. (5.46) it is specifically assumed that $k>k'$. The reasoning is, of course, more general and holds also if $k\leq k'$.

noting that $n_k, n_{k'} \in \{0,1\}$, with $\mathcal{N} = n_{k'} + \ldots + n_{k-1}$ in the special case $k' < k$ (and similarly for $k' > k$) corresponding to the number of nearest-neighbour transpositions that are needed for the re-ordering of the quantum numbers $k_1, \ldots, k, \ldots, k_N$.

5.4 The Fock space

Instead of elaborating along the above lines how to represent the operator $\hat{A}$ within the symmetric or antisymmetric basis $\mathcal{B}_N^{\pm}$, we shall now introduce a framework that strongly facilitates such representations. To this end, we first introduce a new notation for the basis states of $\mathcal{B}_N^{\pm}$, namely

$$|\phi^{\pm}_{k_1 \cdots k_N}\rangle \equiv |n_0, n_1, n_2, \ldots\rangle_{\pm} \tag{5.49}$$

where n_k is, as defined above, the occupation number of the individual single-particle basis state $|\phi_k\rangle \in \mathcal{B}_1$. Clearly, a given symmetric or antisymmetric many-body basis state $|\phi^{\pm}_{k_1 \cdots k_N}\rangle$ corresponds to a well-defined and unique set of occupation numbers $n_0, n_1, n_2, \ldots \in \mathbb{N}_0$ for bosons and $n_0, n_1, n_2, \ldots \in \{0,1\}$ for fermions. Conversely, each combination of occupation numbers $n_0, n_1, n_2, \ldots$ corresponds to a well-defined bosonic or fermionic (the latter only if $n_k \in \{0,1\}$ for all k) basis state $|\phi^{\pm}_{k_1 \cdots k_N}\rangle \in \mathcal{B}_N^{\pm}$ with $N = \sum_{k=0}^{\infty} n_k$. The state $|n_0, n_1, n_2, \ldots\rangle_{\pm}$ will be named *Fock state* (with respect to a given single-particle basis $\mathcal{B}_1 = (|\phi_0\rangle, |\phi_1\rangle, |\phi_2\rangle, \ldots)$) in the following.

We then define the *Fock space* for bosons or fermions,

$$\mathcal{H}^{\pm} = \bigoplus_{N=0}^{\infty} \mathcal{H}_N^{\pm} = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \mathcal{H}_2^{\pm} \oplus \mathcal{H}_3^{\pm} \oplus \ldots \,, \tag{5.50}$$

as the direct sum of the individual symmetric or antisymmetric Hilbert spaces $\mathcal{H}_N^{\pm}$ for all possible particle numbers $N \in \mathbb{N}_0$. This Fock space is spanned by the union set

$$\mathcal{B}^{\pm} = \bigcup_{N=0}^{\infty} \mathcal{B}_N^{\pm} = \mathcal{B}_0 \cup \mathcal{B}_1 \cup \mathcal{B}_2^{\pm} \cup \mathcal{B}_3^{\pm} \cup \ldots \tag{5.51}$$

of the individual symmetric or antisymmetric bases

$$\mathcal{B}_N^{\pm} = \left(|n_0, n_1, n_2, \ldots\rangle_{\pm} : \sum_{k=0}^{\infty} n_k = N \right) . \tag{5.52}$$

We then obtain

$$\mathcal{B}^{+} = (|n_0, n_1, n_2, \ldots\rangle_{+} : n_k \in \mathbb{N}_0 \text{ for all } k \in \mathbb{N}_0) \,, \tag{5.53}$$

$$\mathcal{B}^{-} = (|n_0, n_1, n_2, \ldots\rangle_{-} : n_k \in \{0,1\} \text{ for all } k \in \mathbb{N}_0) \tag{5.54}$$

as orthonormal bases for $\mathcal{H}^+$ and $\mathcal{H}^-$, respectively, with

$$ {}_\pm\langle n_0, n_1, n_2, \ldots | n_0', n_1', n_2', \ldots\rangle_\pm = \delta_{n_0 n_0'}\delta_{n_1 n_1'}\delta_{n_2 n_2'}\cdots . \tag{5.55}$$

Obviously, symmetrization or antisymmetrization is not explicitly needed if there are less than two particles; hence $\mathcal{B}_N^+ = \mathcal{B}_N^- \equiv \mathcal{B}_N$ and $\mathcal{H}_N^+ = \mathcal{H}_N^- \equiv \mathcal{H}_N$ for $N = 0$ or 1. The space $\mathcal{H}_0$ is special as it is spanned by one single basis state

$$ |-\rangle \equiv |0, 0, 0, \ldots\rangle \in \mathcal{B}_0 \tag{5.56}$$

of abstract nature (without an associated wavefunction), which corresponds to the absence of particles in the system. It will be named *vacuum state* in the following.

Within the Fock space $\mathcal{H}^\pm$ we can now introduce for each single-particle basis state $|\phi_k\rangle$ so-called *creation and annihilation operators* $\hat{a}_k^\dagger, \hat{a}_k$, which allow us to represent the many-body equivalent of the one-body operator $P_{kk'} = |\phi_k\rangle\langle\phi_{k'}|$ (see Eq. (5.42)) as $\hat{P}_{kk'} = \hat{a}_k^\dagger \hat{a}_k$. For bosons, those new operators are, in accordance with Eqs. (5.46) and (5.47), defined through

$$ \hat{a}_k|n_0, n_1, \ldots, n_k, \ldots\rangle_+ = \sqrt{n_k}|n_0, n_1, \ldots, n_k - 1, \ldots\rangle_+ , \tag{5.57}$$

$$ \hat{a}_k^\dagger|n_0, n_1, \ldots, n_k, \ldots\rangle_+ = \sqrt{n_k + 1}|n_0, n_1, \ldots, n_k + 1, \ldots\rangle_+ \tag{5.58}$$

for each Fock state $|n_0, n_1, \ldots, n_k, \ldots\rangle_+ \in \mathcal{B}^+$. Clearly, $\hat{a}_k^\dagger$ is the adjoint operator of $\hat{a}_k$ as we have

$$ \begin{aligned} {}_+\langle n_0, \ldots, n_k, \ldots | \hat{a}_k^\dagger | n_0', \ldots, n_k', \ldots\rangle_+ &= \sqrt{n_k' + 1}\,\delta_{n_k, n_k'+1} \prod_{k'\neq k} \delta_{n_{k'}' n_{k'}} \\ = \quad {}_+\langle n_0', \ldots, n_k', \ldots | \hat{a}_k | n_0, \ldots, n_k, \ldots\rangle_+^* &= \sqrt{n_k}\,\delta_{n_k', n_k - 1} \prod_{k'\neq k} \delta_{n_{k'}' n_{k'}} \end{aligned} \tag{5.59}$$

for all $|n_0, \ldots, n_k, \ldots\rangle_+, |n_0', \ldots, n_k', \ldots\rangle_+ \in \mathcal{B}^+$. If $n_k = 0$, we obtain from Eq. (5.57) $\hat{a}_k|n_0, \ldots, n_k = 0, \ldots\rangle_+ = 0$ which corresponds to the null vector of $\mathcal{H}^+$ (which is not to be confused with the vacuum state $|0, 0, 0, \ldots\rangle$). Formally, therefore, $\hat{a}_k^\dagger$ creates an additional particle within the one-body basis state $|\phi_k\rangle$, while $\hat{a}_k$ removes or annihilates a particle within that state. These two operations do not commute. Indeed, we have

$$ \hat{a}_k^\dagger \hat{a}_k|n_0, \ldots, n_k, \ldots\rangle_+ = n_k|n_0, \ldots, n_k, \ldots\rangle_+ , \tag{5.60}$$

$$ \hat{a}_k \hat{a}_k^\dagger|n_0, \ldots, n_k, \ldots\rangle_+ = (n_k + 1)|n_0, \ldots, n_k, \ldots\rangle_+ , \tag{5.61}$$

which after subtraction yields $\hat{a}_k\hat{a}_k^\dagger - \hat{a}_k^\dagger\hat{a}_k = 1$ (*i.e.* the identity transformation) for all $k \in \mathbb{N}_0$.

In the case of fermions[3], we define in accordance with Eqs. (5.46) and (5.48)

$$ \hat{a}_k|n_0, \ldots, n_k, \ldots\rangle_- = (-1)^{n_0 + \ldots + n_{k-1}} n_k |n_0, \ldots, n_k - 1, \ldots\rangle_- , \tag{5.62}$$

$$ \hat{a}_k^\dagger|n_0, \ldots, n_k, \ldots\rangle_- = (-1)^{n_0 + \ldots + n_{k-1}} (1 - n_k)|n_0, \ldots, n_k + 1, \ldots\rangle_- , \tag{5.63}$$

[3]In order not to overload the notation, we do make any distinction in the choice of the symbols $\hat{a}_k^\dagger, \hat{a}_k$ for the creation and annihilation operators in the case of bosons or fermions.

which yields $\hat{a}_k|n_0,\ldots,n_k=0,\ldots\rangle_- = 0$ and $\hat{a}_k^\dagger|n_0,\ldots,n_k=1,\ldots\rangle_- = 0$. We have

$$\begin{aligned}\hat{a}_k^\dagger\hat{a}_k|n_0,\ldots,n_k,\ldots\rangle_- &= n_k|n_0,\ldots,n_k,\ldots\rangle_-\,, &(5.64)\\ \hat{a}_k\hat{a}_k^\dagger|n_0,\ldots,n_k,\ldots\rangle_- &= (1-n_k)|n_0,\ldots,n_k,\ldots\rangle_-\,, &(5.65)\end{aligned}$$

which after summation yields $\hat{a}_k\hat{a}_k^\dagger + \hat{a}_k^\dagger\hat{a}_k = 1$ for all $k\in\mathbb{N}_0$. Again, the creation and annihilation operators do not commute. In contrast to the bosonic case, this now holds true also for operators $\hat{a}_k^\dagger, \hat{a}_{k'}$ that are associated with different quantum numbers $k'\neq k$. Considering, without loss of generality, the case $k'>k$, we have

$$\hat{a}_k^\dagger\hat{a}_{k'}|\ldots,n_k,\ldots,n_{k'},\ldots\rangle_- = (-1)^{n_k+\ldots+n_{k'-1}}|\ldots,n_k+1,\ldots,n_{k'}-1,\ldots\rangle_- \quad (5.66)$$

whereas on the other hand

$$\begin{aligned}\hat{a}_{k'}\hat{a}_k^\dagger|\ldots,n_k,\ldots,n_{k'},\ldots\rangle_- &= (-1)^{(n_k+1)+\ldots+n_{k'-1}}|\ldots,n_k+1,\ldots,n_{k'}-1,\ldots\rangle_-\\ &= -\hat{a}_k^\dagger\hat{a}_{k'}|\ldots,n_k,\ldots,n_{k'},\ldots\rangle_-\,, &(5.67)\end{aligned}$$

which yields $\hat{a}_{k'}\hat{a}_k^\dagger + \hat{a}_k^\dagger\hat{a}_{k'} = 0$. Analogous anticommutation relations can be derived in a very similar manner for two creation operators $\hat{a}_k^\dagger, \hat{a}_{k'}^\dagger$ as well as for two annihilation operators $\hat{a}_k, \hat{a}_{k'}$. In particular, we have $\hat{a}_k\hat{a}_k = \hat{a}_k^\dagger\hat{a}_k^\dagger = 0$ for all $k\in\mathbb{N}_0$, which implies that it is not possible to create more than one fermionic particle in the same single-particle state $|\phi_k\rangle$.

Altogether, we then obtain the commutation as well as anticommutation laws

$$[\hat{a}_k, \hat{a}_{k'}^\dagger]_\mp = \delta_{kk'}\,, \quad (5.68)$$

$$[\hat{a}_k, \hat{a}_{k'}]_\mp = [\hat{a}_k^\dagger, \hat{a}_{k'}^\dagger]_\mp = 0 \quad (5.69)$$

for all $k,k'\in\mathbb{N}_0$ in the case of bosons (upper sign) and fermions (lower sign), where we define by

$$\begin{aligned}[A,B]_- \equiv [A,B] &= AB-BA\,, &(5.70)\\ [A,B]_+ \equiv \{A,B\} &= AB+BA &(5.71)\end{aligned}$$

the commutator as well as the anticommutator, respectively, of two operators A and B. In both the bosonic and the fermionic case, the creation operators $\hat{a}_k^\dagger$ can be used in order to generate the Fock states associated with the corresponding single-particle basis $\mathcal{B}_1$. We obtain

$$|n_0,n_1,n_2,\ldots\rangle = \frac{1}{\sqrt{n_0!}}\left(\hat{a}_0^\dagger\right)^{n_0}\frac{1}{\sqrt{n_1!}}\left(\hat{a}_1^\dagger\right)^{n_1}\frac{1}{\sqrt{n_2!}}\left(\hat{a}_2^\dagger\right)^{n_2}\ldots|-\rangle \quad (5.72)$$

where $|-\rangle$ represents the vacuum as defined in Eq. (5.56).

Using Eq. (5.43) as well as $\hat{P}_{kk'} = \hat{a}_k^\dagger \hat{a}_{k'}$, we are now in a position to represent the many-body equivalent associated with the one-body operator $A : \mathcal{H}_1 \to \mathcal{H}_1$ for both bosons and fermions as

$$\hat{A} = \sum_{k,k'=0}^{\infty} A_{kk'} \hat{a}_k^\dagger \hat{a}_{k'} \tag{5.73}$$

with $A_{kk'} = \langle \phi_k | A | \phi_{k'} \rangle$. The combination of one creation with one annihilation operator within Eq. (5.73) ensures that $\hat{A}$ does not change the total number of particles when being applied to a Fock state. $\hat{A}$ therefore represents an endomorphism within the subspaces $\mathcal{H}_N^\pm$ of the Fock space, in contrast to $\hat{a}_k$ and $\hat{a}_k^\dagger$ which transform an element of $\mathcal{H}_N^\pm$ to $\mathcal{H}_{N-1}^\pm$ and $\mathcal{H}_{N+1}^\pm$, respectively. A particularly relevant one-body operator is the projector $P_{kk} = |\phi_k\rangle\langle\phi_k|$ onto the single-particle state ϕ_k. Its many-body equivalent $\hat{n}_k \equiv \hat{P}_{kk} = \hat{a}_k^\dagger \hat{a}_k$ is named *occupation number operator* associated with $|\phi_k\rangle$, since its eigenvalues are, for both bosons (5.60) and fermions (5.64), given by the occupation numbers n_k of the state $|\phi_k\rangle$. The sum $\hat{N} = \sum_k \hat{n}_k$ of those occupation number operators yields the total number of particles N in the system, independently of the chosen single-particle basis $\mathcal{B}_1$.

The concept of total operators within a many-particle space can be applied also for *two-body* operators $B : \mathcal{H}_2 \to \mathcal{H}_2$. A prominent physical example is the electrostatic interaction energy of two electrons, whose associated two-body operator reads

$$U(\mathbf{r}_1, \mathbf{r}_2) = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \tag{5.74}$$

in position representation, with $\mathbf{r}_1$ and $\mathbf{r_2}$ denoting the positions of two interacting electrons. It is well known that the total electrostatic interaction energy of a system of N electron situated at the positions $\mathbf{r}_1, \ldots, \mathbf{r_N}$ is then given by

$$U(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \frac{1}{2} \sum_{i \neq j = 1}^{N} U(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{2} \sum_{i \neq j = 1}^{N} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \tag{5.75}$$

where the factor $1/2$ in Eq. (5.75) in introduced in order to avoid double countings of pairs of electrons.

Most generally, we can represent a two-body operator B within the single-particle basis $\mathcal{B}_1$ as

$$B = \sum_{k_1, k_1' = 0}^{\infty} \sum_{k_2, k_2' = 0}^{\infty} B_{k_1 k_2 k_1' k_2'} |\phi_{k_1} \phi_{k_2}\rangle\langle\phi_{k_1'} \phi_{k_2'}| \tag{5.76}$$

with $B_{k_1 k_2 k_1' k_2'} = \langle \phi_{k_1} \phi_{k_2} | B | \phi_{k_1'} \phi_{k_2'} \rangle = B_{k_2 k_1 k_2' k_1'}$ for indistinguishable particles. The associated total operator in the Fock space can then be shown to be given by

$$\hat{B} = \frac{1}{2} \sum_{k_1, k_1' = 0}^{\infty} \sum_{k_2, k_2' = 0}^{\infty} B_{k_1 k_2 k_1' k_2'} \hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger \hat{a}_{k_2'} \hat{a}_{k_1'} \tag{5.77}$$

for both bosons and fermions. Similarly, three-body operators $C : \mathcal{H}_3 \to \mathcal{H}_3$ given by

$$C = \sum_{k_1,k_1'=0}^{\infty} \sum_{k_2,k_2'=0}^{\infty} \sum_{k_3,k_3'=0}^{\infty} C_{k_1k_2k_3k_1'k_2'k_3'} |\phi_{k_1}\phi_{k_2}\phi_{k_3}\rangle\langle\phi_{k_1'}\phi_{k_2'}\phi_{k_3'}| \tag{5.78}$$

with $C_{k_1k_2k_3k_1'k_2'k_3'} = \langle\phi_{k_1}\phi_{k_2}\phi_{k_3}|C|\phi_{k_1'}\phi_{k_2'}\phi_{k_3'}\rangle$ are represented in the Fock space through their associated total operators

$$\hat{C} = \frac{1}{3!} \sum_{k_1,k_1'=0}^{\infty} \sum_{k_2,k_2'=0}^{\infty} \sum_{k_3,k_3'=0}^{\infty} C_{k_1k_2k_3k_1'k_2'k_3'} \hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger \hat{a}_{k_3}^\dagger \hat{a}_{k_3'} \hat{a}_{k_2'} \hat{a}_{k_1'} \,, \tag{5.79}$$

where the prefactor 1/3! accounts for multiple countings of triples of particles.

5.5 The field operator

Evidently, the notion of Fock states, given by Eq. (5.49), as well as the definition of the associated creation and annihilation operators are intimately linked to a specific choice for the single-particle basis $\mathcal{B}_1$. Changing this basis will necessarily give rise to different creation and annihilation operators and thereby also, by virtue of Eq. (5.72), to different Fock states.

Let us specifically introduce by

$$\mathcal{B}_1' = (|\chi_l\rangle)_{l\in\mathbb{N}_0} = (|\chi_0\rangle, |\chi_1\rangle, |\chi_2\rangle, \ldots) \tag{5.80}$$

another orthonormal basis of $\mathcal{H}_1$. The new basis states can be represented within the old basis $\mathcal{B}_1 = (|\phi_k\rangle)$ through

$$|\chi_l\rangle = \sum_{k=0}^{\infty} U_{kl} |\phi_k\rangle \tag{5.81}$$

with the overlap matrix elements

$$U_{kl} = \langle\phi_k|\chi_l\rangle \,. \tag{5.82}$$

As both $\mathcal{B}_1$ and $\mathcal{B}_1'$ are orthonormal bases, we have $\langle\phi_k|\phi_{k'}\rangle = \delta_{kk'}$ and $\langle\chi_l|\chi_{l'}\rangle = \delta_{ll'}$ which implies

$$\sum_{k=0}^{\infty} U_{kl}^* U_{kl'} = \delta_{ll'} \,, \tag{5.83}$$

i.e., the transformation matrix $U \equiv (U_{kl})_{k,l\in\mathbb{N}_0} = (U^\dagger)^{-1}$ is unitary. We can therefore invert the basis transformation (5.81) by

$$|\phi_k\rangle = \sum_{l=0}^{\infty} U_{kl}^* |\chi_l\rangle \tag{5.84}$$

and obtain likewise

$$\sum_{l=0}^{\infty} U_{kl} U_{k'l}^* = \delta_{kk'} \,. \tag{5.85}$$

Using this new basis $\mathcal{B}_1'$, the fully symmetrized and antisymmetrized basis states of the bosonic and fermionic Hilbert spaces $\mathcal{H}_N^{\pm}$ can, in perfect analogy with Eqs. (5.40), (5.49), and (5.72), be expressed as

$$\begin{aligned} |\chi^{\pm}_{l_1 \cdots l_N}\rangle &= \frac{1}{\sqrt{N! \prod_{l=0}^{\infty} \nu_l!}} \sum_{\pi \in \Pi_N} (\pm 1)^{\pi} |\chi_{l_{\pi(1)}} \cdots \chi_{l_{\pi(N)}}\rangle & (5.86) \\ &= |\nu_0, \nu_1, \nu_2, \ldots\rangle & (5.87) \\ &= \frac{1}{\sqrt{\nu_0!}} \left(\hat{b}_0^{\dagger}\right)^{\nu_0} \frac{1}{\sqrt{\nu_1!}} \left(\hat{b}_1^{\dagger}\right)^{\nu_1} \frac{1}{\sqrt{\nu_2!}} \left(\hat{b}_2^{\dagger}\right)^{\nu_2} \ldots |-\rangle & (5.88) \end{aligned}$$

with $\nu_l \in \mathbb{N}_0$ for bosons and $\nu_l \in \{0, 1\}$ for fermions being the occupation number of the single-particle state $|\chi_l\rangle$. $\hat{b}_l^{\dagger}$ and $\hat{b}_l$ are the creation and annihilation operators associated with the state $|\chi_l\rangle$ which are defined in perfect analogy with Eqs. (5.57) and (5.58) for bosons and with Eqs. (5.62) and (5.63) for fermions. Comparing the expressions (5.88) and (5.72) for the special case of one single particle with the relations (5.81) and (5.84) between the old and new basis states, we immediately infer

$$\hat{b}_l^{\dagger} = \sum_{k=0}^{\infty} U_{kl} \hat{a}_k^{\dagger} \quad \text{or, equivalently,} \quad \hat{b}_l = \sum_{k=0}^{\infty} U_{kl}^* \hat{a}_k \tag{5.89}$$

as well as

$$\hat{a}_k^{\dagger} = \sum_{l=0}^{\infty} U_{kl}^* \hat{b}_l^{\dagger} \quad \text{or, equivalently,} \quad \hat{a}_k = \sum_{l=0}^{\infty} U_{kl} \hat{b}_l \,. \tag{5.90}$$

One-body operators $A : \mathcal{H}_1 \to \mathcal{H}_1$ are then represented as

$$\hat{A} = \sum_{k,k'=0}^{\infty} \langle \phi_k | A | \phi_{k'} \rangle \hat{a}_k^{\dagger} \hat{a}_{k'} = \sum_{l,l'=0}^{\infty} \langle \chi_l | A | \chi_{l'} \rangle \hat{b}_l^{\dagger} \hat{b}_{l'} \tag{5.91}$$

in the Fock space. By virtue of the unitarity of the basis transformation expressed by Eq. (5.83), we then obtain the same commutation or anticommutation laws,

$$[\hat{b}_l, \hat{b}_{l'}^{\dagger}]_{\mp} = \delta_{ll'} \,, \tag{5.92}$$

$$[\hat{b}_l, \hat{b}_{l'}]_{\mp} = [\hat{b}_l^{\dagger}, \hat{b}_{l'}^{\dagger}]_{\mp} = 0 \,, \tag{5.93}$$

as for the old creation and annihilation operators $\hat{a}_k^{\dagger}, \hat{a}_k$.

We now consider the *continuous* single-particle basis

$$\tilde{\mathcal{B}}_1 = (|\xi\rangle) \equiv (|\mathbf{r}\sigma\rangle)_{\mathbf{r} \in \mathbb{R}^3, \sigma \in I} \tag{5.94}$$

which contains the eigenstates $|\xi\rangle \equiv |\mathbf{r}\sigma\rangle$ of the position and spin operators. The continuous analog of the overlap matrix elements U_{kl}^* is now given by the wavefunctions $\phi_k(\mathbf{r}\sigma) \equiv \langle \mathbf{r}\sigma|\phi_k\rangle$ that are associated with the states $|\phi_k\rangle$. In analogy with Eqs. (5.81) and (5.84), the transformations between the discrete basis $\mathcal{B}_1$ and the continuous basis $\tilde{\mathcal{B}}_1$ are expressed through the relations

$$|\mathbf{r}\sigma\rangle = \sum_{k=0}^{\infty} \phi_k^*(\mathbf{r}\sigma)|\phi_k\rangle\,, \tag{5.95}$$

$$|\phi_k\rangle = \sum_{\sigma\in I} \int d^3r \phi_k(\mathbf{r}\sigma)|\mathbf{r}\sigma\rangle\,. \tag{5.96}$$

The orthogonality relations (5.83) and (5.85) now read

$$\sum_{k=0}^{\infty} \phi_k \mathbf{r}\sigma)\phi_k^*(\mathbf{r}'\sigma') = \delta_{\sigma\sigma'}\delta(\mathbf{r}-\mathbf{r}')\,, \tag{5.97}$$

$$\sum_{\sigma\in I} \int d^3r \phi_k^*(\mathbf{r}\sigma)\phi_{k'}(\mathbf{r}\sigma) = \delta_{kk'}\,, \tag{5.98}$$

respectively, *i.e.* they describe the orthogonality (5.98) and completeness (5.97) of the single-particle basis $\mathcal{B}_1$.

The *field operators* are now introduced as the creation and annihilation operators $\hat{\psi}_\sigma^\dagger(\mathbf{r}), \hat{\psi}_\sigma(\mathbf{r})$ that are associated with this continuous basis $\tilde{\mathcal{B}}_1$. $\hat{\psi}_\sigma^\dagger(\mathbf{r})$ creates a particle with spin σ at position $\mathbf{r}$, while $\hat{\psi}_\sigma(\mathbf{r})$ annihilates such a particle at $\mathbf{r}$. In analogy with Eq. (5.89), we can define these operators through

$$\hat{\psi}_\sigma(\mathbf{r}) = \sum_{k=0}^{\infty} \phi_k(\mathbf{r}\sigma)\hat{a}_k \quad \text{or, equivalently,} \quad \hat{\psi}_\sigma^\dagger(\mathbf{r}) = \sum_{k=0}^{\infty} \phi_k^*(\mathbf{r}\sigma)\hat{a}_k^\dagger\,. \tag{5.99}$$

Conversely, the creation and annihilation operators $\hat{a}_k^\dagger, \hat{a}_k$ associated with the basis state $|\phi_k\rangle$ can be expressed in terms of the field operators according to

$$\hat{a}_k = \sum_{\sigma\in I} \int d^3r \phi_k^*(\mathbf{r}\sigma)\hat{\psi}_\sigma(\mathbf{r}) \quad \text{or, equivalently,} \quad \hat{a}_k^\dagger = \sum_{\sigma\in I} \int d^3r \phi_k(\mathbf{r}\sigma)\hat{\psi}_\sigma^\dagger(\mathbf{r}) \tag{5.100}$$

in analogy with Eq. (5.90). Using Eq. (5.99), the commutation or anticommutation relations (5.68) and (5.69) for the operators $\hat{a}_k$ and $\hat{a}_k^\dagger$, as well as the completeness relation (5.97), we obtain the commutation and anticommutation laws

$$[\hat{\psi}_\sigma(\mathbf{r}), \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}')]_\mp = \delta_{\sigma\sigma'}\delta(\mathbf{r}-\mathbf{r}')\,, \tag{5.101}$$

$$[\hat{\psi}_\sigma(\mathbf{r}), \hat{\psi}_{\sigma'}(\mathbf{r}')]_\mp = [\hat{\psi}_\sigma^\dagger(\mathbf{r}), \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}')]_\mp = 0 \tag{5.102}$$

for bosons and fermions, respectively. The operator that counts the total number of particles in the system can now be expressed as

$$\hat{N} = \sum_{k=0}^{\infty} \hat{a}_k^\dagger \hat{a}_k = \sum_{\sigma \in I} \int d^3 r \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) \tag{5.103}$$

where $\hat{\psi}_\sigma^\dagger(\mathbf{r})\hat{\psi}_\sigma(\mathbf{r})$ represents the density operator of particles with spin σ at the position $\mathbf{r}$. In the case of fermions we have $\hat{\psi}_\sigma^\dagger(\mathbf{r})\hat{\psi}_\sigma^\dagger(\mathbf{r}) = \hat{\psi}_\sigma(\mathbf{r})\hat{\psi}_\sigma(\mathbf{r}) = 0$ for all $\mathbf{r} \in \mathbb{R}^3$ and $\sigma \in I$, which expresses again the Pauli exclusion principle stating that two fermionic particles with the same spin σ cannot be encountered at the same position $\mathbf{r}$.

The use of field operators is particularly convenient for the representation of one- or two-body operators within the bosonic or fermionic many-body space. Let us consider the one-body operator

$$A = \sum_{k,k'=0}^{\infty} A_{kk'} |\phi_k\rangle\langle\phi_{k'}| \tag{5.104}$$

with its matrix elements being given by

$$A_{kk'} = \langle\phi_k|A|\phi_{k'}\rangle = \sum_{\sigma \in I} \int d^3 r \phi_k^*(\mathbf{r}\sigma) A \phi_{k'}(\mathbf{r}\sigma)\,. \tag{5.105}$$

Using Eqs. (5.105) and (5.99), we can express its many-body equivalent as

$$\hat{A} = \sum_{k,k'=0}^{\infty} A_{kk'} \hat{a}_k^\dagger \hat{a}_{k'} = \sum_{\sigma \in I} \int d^3 r \hat{\psi}_\sigma^\dagger(\mathbf{r}) A \hat{\psi}_\sigma(\mathbf{r}) \tag{5.106}$$

where on the right-hand side of Eq. (5.106) the one-body operator A acts on the spatial dependence and the spin component of field operator $\hat{\psi}_\sigma(\mathbf{r})$ in the same way as it would for an ordinary wavefunction. Hence, the many-body equivalent associated with a given one-body operator is obtained by writing down the expression for the expectation value of this operator within the wavefunction $\psi \equiv \psi_\sigma(\mathbf{r})$ and then replacing $\psi_\sigma(\mathbf{r})$ with $\hat{\psi}_\sigma(\mathbf{r})$ and $\psi_\sigma^*(\mathbf{r})$ with $\hat{\psi}_\sigma^\dagger(\mathbf{r})$.

Similarly, the many-body equivalent of the two-body operator

$$B = \sum_{k_1,k_1'=0}^{\infty} \sum_{k_2,k_2'=0}^{\infty} B_{k_1 k_2 k_1' k_2'} |\phi_{k_1}\phi_{k_2}\rangle\langle\phi_{k_1'}\phi_{k_2'}| \tag{5.107}$$

with

$$\begin{aligned} B_{k_1 k_2 k_1' k_2'} &= \langle\phi_{k_1}\phi_{k_2}|B|\phi_{k_1'}\phi_{k_2'}\rangle \qquad (5.108)\\ &= \sum_{\sigma_1,\sigma_2 \in I} \int d^3 r_1 \int d^3 r_2 \phi_{k_1}^*(\mathbf{r}_1\sigma_1)\phi_{k_2}^*(\mathbf{r}_2\sigma_2) B \phi_{k_2'}(\mathbf{r}_2\sigma_2)\phi_{k_1'}(\mathbf{r}_1\sigma_1) \end{aligned}$$

can be expressed as

$$\hat{B} = \frac{1}{2}\sum_{k_1,k_1'=0}^{\infty}\sum_{k_2,k_2'=0}^{\infty} B_{k_1k_2k_1'k_2'}\hat{a}_{k_1}^{\dagger}\hat{a}_{k_2}^{\dagger}\hat{a}_{k_2'}\hat{a}_{k_1'} \tag{5.109}$$

$$= \frac{1}{2}\sum_{\sigma_1,\sigma_2\in I}\int d^3r_1\int d^3r_2\hat{\psi}_{\sigma_1}^{\dagger}(\mathbf{r}_1)\hat{\psi}_{\sigma_2}^{\dagger}(\mathbf{r}_2)B\hat{\psi}_{\sigma_2}(\mathbf{r}_2)\hat{\psi}_{\sigma_1}(\mathbf{r}_1)\,. \tag{5.110}$$

In the special case of a two-body interaction potential $U \equiv U(\mathbf{r}_1,\mathbf{r}_2) = U(\mathbf{r}_2,\mathbf{r}_1)$, we obtain the associated operator in the Fock space

$$\hat{U} = \frac{1}{2}\sum_{\sigma_1,\sigma_2\in I}\int d^3r_1\int d^3r_2 U(\mathbf{r}_1,\mathbf{r}_2)\hat{\psi}_{\sigma_1}^{\dagger}(\mathbf{r}_1)\hat{\psi}_{\sigma_2}^{\dagger}(\mathbf{r}_2)\hat{\psi}_{\sigma_2}(\mathbf{r}_2)\hat{\psi}_{\sigma_1}(\mathbf{r}_1) \tag{5.111}$$

which can be seen as a straightforward quantum analog of the classical expression (5.75) for the total interaction energy. Indeed, as in Eq. (5.75) the prefactor $1/2$ compensates for double countings of interaction energies between two particles, while the specific order of the creation and annihiliation operators in Eq. (5.111) ensures that artificial self-interaction terms, in which a given particle would appear to interact with itself (corresponding to the excluded case $i = j$ in Eq. (5.75)), are not counted for the total interaction energy. Together with the kinetic energy and the confinement of the particles within the external potential $V(\mathbf{r})$, the many-body Hamiltonian of a system of N indistinguishable bosonic or fermionic particles with mass m that interact via $U(\mathbf{r}_1,\mathbf{r}_2)$ is then written as

$$\hat{H} = \sum_{\sigma\in I}\int d^3r\hat{\psi}_{\sigma}^{\dagger}(\mathbf{r})\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}^2}+V(\mathbf{r})\right)\hat{\psi}_{\sigma}(\mathbf{r}) \tag{5.112}$$

$$+\frac{1}{2}\sum_{\sigma_1,\sigma_2\in I}\int d^3r_1\int d^3r_2 U(\mathbf{r}_1,\mathbf{r}_2)\hat{\psi}_{\sigma_1}^{\dagger}(\mathbf{r}_1)\hat{\psi}_{\sigma_2}^{\dagger}(\mathbf{r}_2)\hat{\psi}_{\sigma_2}(\mathbf{r}_2)\hat{\psi}_{\sigma_1}(\mathbf{r}_1)\,.$$

Chapter 6

Approximate methods for the ground state

6.1 The variational principle

We now address the question how to determine the ground state of the Hamiltonian that describes a given many-body system. Indeed, the ground state of a many-body system plays a particularly relevant role in a number of physical contexts. Atoms and molecules, for instance, are, at not too high temperatures, mostly encountered in their ground states concerning the electronic degrees of freedom. Hence, a reliable numerical representation of the electronic ground state is needed for the quantitative description of a number of dynamical processes involving atoms and molecules, such as atomic collision, molecular vibration and rotation, as well as laser-induced electronic excitation starting from the ground state of an atom or molecule, to mention some examples.

Apart from a few exotic special cases, it is not possible to determine by analytical means the ground state or any other eigenstate of the Hamiltonian describing an interacting many-body system. From the numerical point of view, one can try to compute those eigenstates by a diagonalization of the Hamiltonian matrix that is obtained within a truncated basis of the many-body Hilbert space. This procedure, however, can be computationally extremely expensive since the dimension of the thereby obtained matrix scales approximately as $\sim L^N$ where L is the number of single-particle eigenstates considered within the truncated basis and N is the number of particles.

On the other hand, the ground state is rather special within the many-body eigenbasis of the Hamiltonian insofar as it corresponds to its lowest eigenenergy. This specific property is exploited within the variational principle. The latter states that for any Hamiltonian $\hat{H}$ the eigenspectrum of which is bounded from below (*i.e.*, for any Hamiltonian that actually has a ground state), the (normal-

ized) ground state $|\phi_0\rangle$ is characterized by the property

$$E_0 = \langle\phi_0|\hat{H}|\phi_0\rangle \leq \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \tag{6.1}$$

for all $\psi \in \mathcal{H}$ where $\mathcal{H}$ is the Hilbert space of the quantum system. This yields the ground state energy

$$E_0 = \min_{\psi\in\mathcal{H}} \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \tag{6.2}$$

as the lower bound of the expectation value of the Hamiltonian within any normalized state ψ of the many-body system.

This particular property can be straightforwardly proven for the case of a Hamiltonian $\hat{H}$ with a discrete spectrum[1]. Let us denote by $|\phi_n\rangle$ the eigenstates of the Hamiltonian, satisfying $\langle\phi_n|\phi_{n'}\rangle = \delta_{nn'}$ for all $n, n' \in \mathbb{N}_0$, and the corresponding eigenenergies by E_n. Any state ψ of the Hilbert space can then be represented within this eigenbasis of the Hamiltonian through a linear combination $|\psi\rangle = \sum_{n=0}^{\infty} C_n|\phi_n\rangle$ with complex coefficients $C_n \in \mathbb{C}$. As $\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle$ by definition, we then obtain

$$\langle\psi|\hat{H}|\psi\rangle = \sum_{n=0}^{\infty} |C_n|^2 E_n \geq E_0 \sum_{n=0}^{\infty} |C_n|^2 = E_0\langle\psi|\psi\rangle \tag{6.3}$$

using the fact that $E_n \geq E_0$ for all $n \in \mathbb{N}_0$.

In practice, one can start with a reasonably good first approximation $|\psi\rangle$ to the ground state $|\phi_0\rangle$ and then try to improve this approximation and eventually obtain $|\phi_0\rangle$ by minimizing the right-hand side of Eq. (6.1) under variations of ψ. Those variations can, in general, not be carried out within the entire many-body Hilbert space. A common strategy consists then in restricting the variations of ψ to a convenient subspace or submanifold of $\mathcal{H}$ within which the resulting minimization procedure becomes numerically tractable. While this procedure does, in general, not yield the exact ground state, one nevertheless obtains an improved approximation $\tilde{\psi}$ to the ground state as compared to the initial guess ψ, insofar as the new approximation $\tilde{\psi}$ generally satisfies the relation

$$\frac{\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} \leq \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}\,. \tag{6.4}$$

This new approximation thereby yields a refined upper bound for the exact ground state energy E_0 by virtue of Eq. (6.2).

To demonstrate how the variational principle can be applied in practice, let us consider the simple case of a single particle in one spatial dimension governed

[1]The proof for a partially discrete and partially continuous spectrum follows a similar reasoning, but requires a more tedious formulation.

by the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 + \alpha x^4 \tag{6.5}$$

with $m, \omega, \alpha > 0$. Obviously, for $\alpha = 0$ we obtain the Hamiltonian associated with a harmonic oscillator the ground state of which corresponds to a normalized Gaussian wavefunction. For not too strong $\alpha > 0$, we can make the ansatz that the ground state wavefunction is still very well approximated by a normalized Gaussian

$$\phi_0(x) \simeq \frac{1}{\sqrt{\sqrt{\pi}a}} \exp\left(-\frac{x^2}{2a^2}\right) \equiv \phi_0^{(a)}(x) \tag{6.6}$$

whose width $a > 0$ is varied in order to minimize the expectation value of the Hamiltonian. The latter is calculated as

$$E_0^{(a)} \equiv \langle \phi_0^{(a)} | \hat{H} | \phi_0^{(a)} \rangle = \frac{\hbar^2}{4ma^2} + \frac{1}{4}m\omega^2 a^2 + \frac{3}{4}\alpha a^4 \,. \tag{6.7}$$

As $E_0^{(a)}$ clearly diverges for $a \to 0$ and $a \to \infty$, it exhibits a global minimum at some finite $a > 0$ at which we have $\frac{d}{da}E_0^{(a)} = 0$. This yields the equation

$$a^4 = \frac{\hbar^2}{m^2\omega^2} - \frac{6\alpha}{m\omega^2}a^6 \,. \tag{6.8}$$

In the presence of a weak quartic confinement with $0 < \alpha < m^2\omega^3/(9\sqrt{3}\hbar)$ we obtain

$$a = \sqrt{\frac{m\omega^2}{36\alpha}}\sqrt{(1 - i\sqrt{3})\gamma + (1 + i\sqrt{3})\gamma^{-1} - 2} \tag{6.9}$$

with

$$\gamma = \left(1 - 486\frac{\hbar^2\alpha^2}{m^4\omega^6} + 18\sqrt{3}i\frac{\hbar\alpha}{m^2\omega^3}\sqrt{1 - 243\frac{\hbar^2\alpha^2}{m^4\omega^6}}\right)^{1/3} \tag{6.10}$$

as optimal choice for the width of the Gaussian, which simplifies to

$$a \simeq \sqrt{\frac{\hbar}{m\omega}}\left(1 - \frac{6\hbar\alpha}{m^2\omega^3} + \mathcal{O}(\alpha^2)\right)^{1/4} \tag{6.11}$$

in linear order in α.

6.2 The Hartree appxroximation

We are now considering a system of N indistinguishable bosonic particles with mass m and without spin, which are confined within the (one-body) potential

$V(\mathbf{r})$ and interact via the (two-body) interaction energy $U(\mathbf{r}-\mathbf{r}') = U(\mathbf{r}'-\mathbf{r})$. The Hamiltonian of this system reads

$$\hat{H} = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r_i^2} + V(\mathbf{r}_i)\right) + \frac{1}{2}\sum_{i\neq j=1}^{N} U(\mathbf{r}_i - \mathbf{r}_j)\,. \tag{6.12}$$

In the absence of interaction, *i.e.* for $U \equiv 0$, the eigenstates of the many-body Hamiltonian would be directly given by the Fock states $|n_0, n_1, \ldots\rangle$ associated with the single-particle eigenbasis of the one-body kinetic-plus-potential Hamiltonian. Evidently, the many-body ground state $|\Phi_0\rangle$ of $\hat{H}$ is then obtained by putting all particles in the energetically lowest eigenstate $|\phi_0\rangle$ of the one-body Hamiltonian. In that case, all particles of the system would share the same single-particle wavefunction (or *orbital* as we shall also name it in the following) $\phi_0(\mathbf{r})$.

In the framework of the *Hartree approximation*, we assume this to be the case also in the presence of a non-vanishing (but not too strong) particle-particle interaction. That is, the particles of the system are still supposed to share the same single-particle orbital ϕ_0 for $U \not\equiv 0$. This latter orbital, however, is no longer firmly identified with the ground state of the one-body Hamiltonian, but is varied and optimized in order to minimize the expectation value of the many-body Hamiltonian according to the variational principle.

Choosing a single-particle basis $\mathcal{B}_1 = (|\phi_k\rangle)_{k\in\mathbb{N}_0} = (|\phi_0\rangle, |\phi_1\rangle, \ldots)$ that contains as first element the (normalized) orbital ϕ_0 to be determined, and introducing the associated creation and annihilation operators $\hat{a}_k^\dagger, \hat{a}_k$, we can express the many-body ground state of the system as

$$|\Phi_0\rangle = \frac{1}{\sqrt{N!}}\left(\hat{a}_0^\dagger\right)^N |-\rangle = |N, 0, 0, \ldots\rangle\,. \tag{6.13}$$

Rewriting the Hamiltonian (6.12) as

$$\begin{aligned}\hat{H} &= \int d^3r \hat{\psi}^\dagger(\mathbf{r})\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{r}^2} + V(\mathbf{r})\right)\hat{\psi}(\mathbf{r}) \\ &\quad + \frac{1}{2}\int d^3r_1 \int d^3r_2 U(\mathbf{r}_1 - \mathbf{r}_2)\hat{\psi}^\dagger(\mathbf{r}_1)\hat{\psi}^\dagger(\mathbf{r}_2)\hat{\psi}(\mathbf{r}_2)\hat{\psi}(\mathbf{r}_1)\end{aligned} \tag{6.14}$$

using the field operators $\hat{\psi}(\mathbf{r}) = \sum_{k=0}^{\infty}\phi_k(\mathbf{r})\hat{a}_k$ and $\hat{\psi}^\dagger(\mathbf{r}) = \sum_{k=0}^{\infty}\phi_k^*(\mathbf{r})\hat{a}_k^\dagger$ in accordance with Eqs. (5.99) and (5.112), and evaluating the matrix elements

$$\langle\Phi_0|\hat{a}_k^\dagger\hat{a}_{k'}|\Phi_0\rangle = N\delta_{k0}\delta_{k'0}\,, \tag{6.15}$$

$$\langle\Phi_0|\hat{a}_{k_1}^\dagger\hat{a}_{k_2}^\dagger\hat{a}_{k_2'}\hat{a}_{k_1'}|\Phi_0\rangle = N(N-1)\delta_{k_10}\delta_{k_20}\delta_{k_2'0}\delta_{k_1'0}\,, \tag{6.16}$$

we obtain for the expectation value of the many-body Hamiltonian

$$\begin{aligned}E_0 \equiv \langle\Phi_0|\hat{H}|\Phi_0\rangle &= N\int d^3r\phi_0^*(\mathbf{r})\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}^2} + V(\mathbf{r})\right)\phi_0(\mathbf{r}) \\ &\quad + \frac{1}{2}N(N-1)\int d^3r_1\int d^3r_2 U(\mathbf{r}_1-\mathbf{r}_2)|\phi_0(\mathbf{r}_1)|^2|\phi_0(\mathbf{r}_2)|^2\,.\end{aligned} \tag{6.17}$$

We now have to determine the single-particle orbital ϕ_0 such that the functional $E_0 \equiv E_0[\phi_0]$ is minmized. In analogy with the simple example considered in Section 6.1, we calculate for this purpose the functional derivative of E_0 with respect to $\phi_0(\mathbf{r})$ for all $\mathbf{r} \in \mathbb{R}^3$. A complication is introduced by the fact that ϕ_0 represents *a priori* a complex-valued orbital (even though it will turn out at the end of the calculation that this orbital can be chosen to be entirely real, in view of the Hamiltonian (6.12) under consideration). The convenient approach to be applied in this case consists in interpreting $\phi_0(\mathbf{r})$ and $\phi_0^*(\mathbf{r})$ as *independent* complex fields (noting that complex conjugation does not represent an analytic operation) and determining the complex functional derivative of E_0 with respect $\phi_0(\mathbf{r})$ and $\phi_0^*(\mathbf{r})$ separately. Setting those two functional derivatives to zero gives then rise to two different equations for each $\mathbf{r} \in \mathbb{R}^3$ one of which being the complex conjugate of the other one.

To ensure the correct normalization of the single-particle orbital ϕ_0 in this variational method, we apply the technique of *Lagrange multipliers* and vary the functional $E_0[\phi_0] - N\mu(\int d^3r|\phi_0(\mathbf{r})|^2 - 1)$ instead of $E_0[\phi_0]$. The Lagrange multiplier $\mu \in \mathbb{R}$ is considered as an additional variable of the minimization problem, such that calculating the derivative of the functional with respect to μ and setting it to zero yields the correct normalization of ϕ_0 as a constraint. The functional derivative with respect to $\phi_0^*(\mathbf{r})$ then yields

$$\begin{aligned} 0 &= \frac{\delta}{\delta\phi_0^*(\mathbf{r})}\left[N\int d^3r'\phi_0^*(\mathbf{r}')\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}'^2}+V(\mathbf{r}')-\mu\right)\phi_0(\mathbf{r}')+N\right. \\ &\quad \left.+\frac{1}{2}N(N-1)\int d^3r_1\int d^3r_2 U(\mathbf{r}_1-\mathbf{r}_2)|\phi_0(\mathbf{r}_1)|^2|\phi_0(\mathbf{r}_2)|^2\right] \qquad (6.18) \\ &= N\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}^2}+V(\mathbf{r})-\mu+(N-1)\int d^3r' U(\mathbf{r}-\mathbf{r}')|\phi_0(\mathbf{r}')|^2\right)\phi_0(\mathbf{r}) \end{aligned}$$

which is rewritten as

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}^2}+V(\mathbf{r})+\int d^3r' U(\mathbf{r}-\mathbf{r}')(N-1)|\phi_0(\mathbf{r}')|^2\right)\phi_0(\mathbf{r})=\mu\phi_0(\mathbf{r})\,. \quad (6.19)$$

This equation allows for a neat interpretation as being the effective (nonlinear) Schrödinger equation describing an individual particle of this system. Indeed, this particle would, within this Hartree approximation of the many-body ground state, be subject not only to the external potential $V(\mathbf{r})$ but also to an additional effective potential $\int d^3r' U(\mathbf{r}-\mathbf{r}')(N-1)|\phi_0(\mathbf{r}')|^2$ that arise from the interaction with the other $N-1$ particles of the system. In the spirit of this interpretation, μ then represents the total energy of this particle. Note that we do not simply have $E_0[\phi_0] = N\mu$ for the optimized orbital ϕ_0 in the presence of interaction. However, one can show that in the limit of large $N \gg 1$, in which we are safely allowed to set $N-1 \simeq N$, we have $\frac{d}{dN}E_0[\phi_0] \simeq \mu$ if ϕ_0 solves the nonlinear Schrödinger equation (6.19), or, in other words, $dE_0 = \mu dN$. We are therefore entitled to interpret μ as the *chemical potential* of the bosonic system under consideration.

6.3 The Hartree-Fock equations

Let us finally consider a system of N indistinguishable fermions with semi-integer spin. In contrast to the bosonic case treated in the previous section, fermions obey the Pauli exclusion principle, which implies that the many-body ground state of the fermionic system cannot be described by means of only one single-particle state $|\phi_0\rangle$. Historically, Hartree therefore proposed to model the ground state of the fermionic system by means of N orthogonal and normalized single-particle states $|\phi_0\rangle, \ldots, |\phi_{N-1}\rangle$ such that the many-body ground state wavefunction would read $\Phi_0(\xi_1, \ldots, \xi_N) = \phi_0(\xi_1) \cdots \phi_{N-1}(\xi_N)$. This ansatz, however, is not in accordance with the indistinguishability of the particles. It has to undergo entire antisymmetrization in order to be compatible with the symmetry postulate for fermions.

Undertaking such an antisymmetrization, we thereby obtain the *Hartree-Fock approximation* for the ground state $|\Phi_0\rangle$ of the fermionic system. It essentially states that there is an orthonormal basis $\mathcal{B}_1 = (|\phi_k\rangle)_{k\in\mathbb{N}_0} = (|\phi_0\rangle, |\phi_1\rangle, \ldots)$ of the single-particle Hilbert space $\mathcal{H}_1$ such that the ground state of the N-body Hamiltonian is represented as the fermionic Fock state

$$|\Phi_0\rangle = |\phi^-_{N-1,\ldots,1,0}\rangle = |1, 1, \ldots, 1, 0, 0, \ldots\rangle_- = \hat{a}_0^\dagger \hat{a}_1^\dagger \cdots \hat{a}_{N-1}^\dagger |-\rangle \tag{6.20}$$

involving the first N elements $|\phi_0\rangle, |\phi_1\rangle, \ldots, |\phi_{N-1}\rangle$ of the basis $\mathcal{B}_1$. The corresponding ground state wavefunction is then obtained as the Slater determinant

$$\begin{aligned} \langle \xi_1 \cdots \xi_N | \Phi_0 \rangle &= \frac{1}{\sqrt{N!}} \sum_{\pi\in\Pi_N} (\pm 1)^\pi \phi_{\pi(0)}(\xi_1) \cdots \phi_{\pi(N-1)}(\xi_N) && (6.21) \\ &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_0(\xi_1) & \cdots & \phi_{N-1}(\xi_1) \\ \vdots & & \vdots \\ \phi_0(\xi_N) & \cdots & \phi_{N-1}(\xi_N) \end{vmatrix} && (6.22) \end{aligned}$$

and the variational principle consists now in optimizing the single-particle states $\phi_0, \ldots, \phi_{N-1}$ such that the expectation value of the Hamiltonian within this particular approximation of the ground state becomes minimal.

Let us specifically consider the Hamiltonian

$$\hat{H} = \int d\xi \hat{\psi}^\dagger(\xi) H_0 \hat{\psi}(\xi) + \frac{1}{2} \int d\xi_1 \int d\xi_2 U(\xi_1, \xi_2) \hat{\psi}^\dagger(\xi_1) \hat{\psi}^\dagger(\xi_2) \hat{\psi}(\xi_2) \hat{\psi}(\xi_1) \tag{6.23}$$

which contains the hermitian one-body operator $H_0 : \mathcal{H}_1 \to \mathcal{H}_1$ that describes the kinetic energy and an external potential for the particles, as well as the two-body interaction energy $U(\xi_1, \xi_2) = U(\xi_2, \xi_1)$. As usual, the field operators are represented as

$$\hat{\psi}(\xi) = \sum_{k=0}^{\infty} \phi_k(\xi) \hat{a}_k \quad \text{and} \quad \hat{\psi}^\dagger(\xi) = \sum_{k=0}^{\infty} \phi_k^*(\xi) \hat{a}_k^\dagger \tag{6.24}$$

within the single-particle basis $\mathcal{B}_1$. Evaluating

$$\langle\Phi_0|\hat{a}_k^\dagger\hat{a}_{k'}|\Phi_0\rangle = \begin{cases} \delta_{kk'} & \text{if } k < N \\ 0 & \text{otherwise} \end{cases}, \tag{6.25}$$

$$\langle\Phi_0|\hat{a}_{k_1}^\dagger\hat{a}_{k_2}^\dagger\hat{a}_{k_2'}\hat{a}_{k_1'}|\Phi_0\rangle = \begin{cases} \delta_{k_1k_1'}\delta_{k_2k_2'} - \delta_{k_1k_2'}\delta_{k_2k_1'} & \text{if } k_1, k_2 < N \\ 0 & \text{otherwise} \end{cases}, \tag{6.26}$$

we obtain the expectation value

$$\begin{aligned} E_0 \equiv \langle\Phi_0|\hat{H}|\Phi_0\rangle &= \sum_{k=0}^{N-1}\int d\xi\phi_k^*(\xi)H_0\phi_k(\xi) \\ &+\frac{1}{2}\sum_{k_1,k_2=0}^{N-1}\int d\xi_1\int d\xi_2 U(\xi_1,\xi_2)|\phi_{k_1}(\xi_1)|^2|\phi_{k_2}(\xi_2)|^2 \\ &-\frac{1}{2}\sum_{k_1,k_2=0}^{N-1}\int d\xi_1\int d\xi_2 U(\xi_1,\xi_2)\phi_{k_1}^*(\xi_1)\phi_{k_2}(\xi_1)\phi_{k_2}^*(\xi_2)\phi_{k_1}(\xi_2) \end{aligned} \tag{6.27}$$

of the many-body Hamiltonian. The second line of Eq. (6.27) contains the *Hartree term*, which would also result from the simple Hartree approximation $\Phi_0(\xi_1,\ldots,\xi_N) = \phi_0(\xi_1)\cdots\phi_{N-1}(\xi_N)$, while the *Fock term* in the third line of Eq. (6.27) accounts for the antisymmetry of the ground state wavefunction.

We now apply the variational method in order to minimize the energy $E_0 \equiv E_0[\phi_0,\ldots,\phi_{N-1}]$ under the constraint that the wavefunctions $\phi_0,\ldots,\phi_{N-1}$ are properly normalized. This normalization can be ensured by the introduction of N Lagrange multipliers $\epsilon_0,\ldots,\epsilon_{N-1} \in \mathbb{R}$ such that we consider the variation of the functional $E_0[\phi_0,\ldots,\phi_{N-1}] - \sum_{k=0}^{N-1}\epsilon_k(\int d\xi|\phi_k(\xi)|^2 - 1)$ instead of $E_0[\phi_0,\ldots,\phi_{N-1}]$. The functional derivative with respect to $\phi_k^*(\xi)$ then yields

$$\begin{aligned} 0 &= \frac{\delta}{\delta\phi_k^*(\xi)}\left[E_0[\phi_0,\ldots,\phi_{N-1}] - \sum_{k=0}^{N-1}\epsilon_k\left(\int d\xi|\phi_k(\xi)|^2 - 1\right)\right] \\ &= (H_0-\epsilon_k)\phi_k(\xi) + \sum_{k'=0}^{N-1}\int d\xi' U(\xi,\xi')|\phi_{k'}(\xi')|^2\phi_k(\xi) \\ &\quad -\sum_{k'=0}^{N-1}\int d\xi' U(\xi,\xi')\phi_{k'}(\xi)\phi_{k'}^*(\xi')\phi_k(\xi') \end{aligned} \tag{6.28}$$

for all $k = 0,\ldots,N-1$. This set of equations is equivalent to the *Hartree-Fock equations*

$$\left(H_{HF}\phi_k\right)(\xi) = \epsilon_k\phi_k(\xi) \tag{6.29}$$

with

$$\begin{aligned}(H_{HF}\psi)(\xi) &= \left(H_0 + \sum_{k'=0}^{N-1}\int d\xi' U(\xi,\xi')|\phi_{k'}(\xi')|^2\right)\psi(\xi) \\ &\quad - \sum_{k'=0}^{N-1}\int d\xi' U(\xi,\xi')\phi_{k'}(\xi)\phi^*_{k'}(\xi')\psi(\xi')\,. \end{aligned} \tag{6.30}$$

$\phi_0,\ldots,\phi_{N-1}$ are therefore given as eigenstates of the effective (non-local) single-particle Hamiltonian H_{HF}. They are orthogonal by construction as H_{HF} is hermitian. Clearly, in view of minimizing the energy functional $E_0[\phi_0,\ldots,\phi_{N-1}]$, one would choose those eigenstates that exhibit the lowest possible eigenvalues $\epsilon_0 \leq \ldots \leq \epsilon_{N-1}$ within the spectrum of H_{HF}. Again, the effective Hamiltonian H_{HF} parametrically depends on the states ϕ_k to be determined, and we therefore have to find the solutions of a set of nonlinear stationary Schrödinger equations in a self-consistent manner.

Let us now consider the specific case of N electrons with spin 1/2 that are confined within the external potential $V(\mathbf{r})$ and interact via the electrostatic interaction energy

$$U(\mathbf{r}_1-\mathbf{r}_2) = \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1-\mathbf{r}_2|}\,. \tag{6.31}$$

The Hamiltonian of this many-body system reads

$$\begin{aligned}\hat{H} &= \sum_{\sigma=\pm1/2}\int d^3r\hat{\psi}^\dagger_\sigma(\mathbf{r})\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}^2}+V(\mathbf{r})\right)\hat{\psi}_\sigma(\mathbf{r}) \\ &\quad + \frac{1}{2}\sum_{\sigma_1,\sigma_2=\pm1/2}\int d^3r_1\int d^3r_2 U(\mathbf{r}_1-\mathbf{r}_2)\hat{\psi}^\dagger_{\sigma_1}(\mathbf{r}_1)\hat{\psi}^\dagger_{\sigma_2}(\mathbf{r}_2)\hat{\psi}_{\sigma_2}(\mathbf{r}_2)\hat{\psi}_{\sigma_1}(\mathbf{r}_1)\,. \end{aligned} \tag{6.32}$$

As this Hamiltonian is not acting on the spin degree of freedom of the electron (which would be different, *e.g.*, in the presence of a relativistic spin-orbit term), it makes sense to consider a Hartree-Fock approximation in which the electrons occupy single-particle states that have a well-defined spin. We can then rewrite those single-particle states as $|\phi_k\rangle \equiv |\phi_{ls}\rangle$ with $l \equiv l(k) \in \mathbb{N}_0$ being the orbital quantum number and $s \equiv s(k) = \pm 1/2$ being the spin of the state $|\phi_k\rangle$. The corresponding wavefunction then reads

$$\phi_k(\xi) = \phi_{ls}(\mathbf{r}\sigma) = \varphi_l(\mathbf{r})\delta_{\sigma s} \tag{6.33}$$

where $\varphi_l(\mathbf{r})$ is the orbital associated with $|\phi_k\rangle$. The expression (6.24) for the electronic field operators can then be written as

$$\hat{\psi}_\sigma(\mathbf{r}) = \sum_{l=0}^{\infty}\varphi_l(\mathbf{r})\hat{a}_{l\sigma} \quad \text{and} \quad \hat{\psi}^\dagger_\sigma(\mathbf{r}) = \sum_{k=0}^{\infty}\varphi^*_l(\mathbf{r})\hat{a}^\dagger_{l\sigma} \tag{6.34}$$

where the operators $\hat{a}^\dagger_{l\sigma}, \hat{a}_{l\sigma}$ respectively create and annihilate an electron with spin σ in the orbital φ_l. We then obtain

$$\sum_{\sigma_1,\sigma_2=\pm 1/2} \langle\Phi_0|\hat{\psi}^\dagger_{\sigma_1}(\mathbf{r}_1)\hat{\psi}^\dagger_{\sigma_2}(\mathbf{r}_2)\hat{\psi}_{\sigma_2}(\mathbf{r}_2)\hat{\psi}_{\sigma_1}(\mathbf{r}_1)|\Phi_0\rangle = \tag{6.35}$$

$$= \sum_{k1,k_2=0}^{N-1} \left[|\varphi_{l(k_1)}(\mathbf{r}_1)|^2|\varphi_{l(k_2)}(\mathbf{r}_2)|^2 - \delta_{s(k_1),s(k_2)}\varphi^*_{l(k_1)}(\mathbf{r}_1)\varphi_{l(k_2)}(\mathbf{r}_1)\varphi^*_{l(k_2)}(\mathbf{r}_2)\varphi_{l(k_1)}(\mathbf{r}_2)\right]$$

for the expectation value of the two-body term in the Hamiltonian (6.32). Hence, the Fock term that accounts for the antisymmetry of the ground state wavefunction becomes significant only if the two spins $s(k_1)$ and $s(k_2)$ of the involved single-particle states $|\phi_{k_1}\rangle$ and $|\phi_{k_2}\rangle$ are identical.

Let us first consider the case $N = 2L$ with $L \in \mathbb{N}$, *i.e.*, there is an even number of electrons in the system. As illustrated in the left panel of Fig. 6.1, the most obvious choice for the ground state of the many-body system in the framework of the Hartree-Fock approximation would, in that case, consist in representing this ground state by L orthogonal and normalized orbitals $\varphi_0, \ldots, \varphi_{L-1}$ each of which being occupied by two electrons[2], one with spin $\sigma = +1/2$ and the other one with spin $\sigma = -1/2$. This yields the expectation value

$$\begin{aligned}\langle\Phi_0|\hat{H}|\Phi_0\rangle &= 2\sum_{l=0}^{L-1}\int d^3r\varphi^*_l(\mathbf{r})\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}^2} + V(\mathbf{r})\right)\varphi_l(\mathbf{r}) \\ &\quad +2\sum_{l_1,l_2=0}^{L-1}\int d^3r_1\int d^3r_2 U(\mathbf{r}_1-\mathbf{r}_2)|\varphi_{l_1}(\mathbf{r}_1)|^2|\varphi_{l_2}(\mathbf{r}_2)|^2 \\ &\quad -\sum_{l_1,l_2=0}^{L-1}\int d^3r_1\int d^3r_2 U(\mathbf{r}_1-\mathbf{r}_2)\varphi^*_{l_1}(\mathbf{r}_1)\varphi_{l_2}(\mathbf{r}_1)\varphi^*_{l_2}(\mathbf{r}_2)\varphi_{l_1}(\mathbf{r}_2)\end{aligned} \tag{6.36}$$

of the many-body Hamiltonian (6.32), where the numerical prefactors in front of the individual contributions arise from the simple summations over the spin degree of freedom (keeping in mind that the Fock term in the third line requires an identical spin of the two involved electrons). We then obtain the Hartree-Fock equations

$$\begin{aligned}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}^2} + V(\mathbf{r}) + 2\sum_{l'=0}^{L-1}\int d^3r' U(\mathbf{r}-\mathbf{r}')|\varphi_{l'}(\mathbf{r}')|^2\right)\varphi_l(\mathbf{r}) \\ -\sum_{l'=0}^{L-1}\int d^3r' U(\mathbf{r}-\mathbf{r}')\varphi_{l'}(\mathbf{r})\varphi^*_{l'}(\mathbf{r}')\varphi_l(\mathbf{r}') &= \epsilon_l\varphi_l(\mathbf{r})\end{aligned} \tag{6.37}$$

to be solved for $l = 0, \ldots, L-1$ in a self-consistent manner.

[2]This might be different for some many-electron atoms in the presence of spin-orbit and magnetic electron-electron interactions, for which Hund's rule predicts that degenerate subshells should first be populated with a single choice for the spin.

Figure 6.1: Schematic representation of the Hartree-Fock approximation to the ground state of a system containing an even ($N = 6$, left panel) or an odd number ($N = 7$, right panel) of electrons. The horizontal lines represent the levels that correspond to the eigenvalues ϵ_l of the Hartree-Fock Hamiltonian. In the even case, the $N/2$ energetically lowest single-particle orbitals are populated with two electrons per orbital, one with "spin up" and the other one with "spin down". In the odd case, one additional orbital is populated with the extra electron that can have either spin up or spin down.

In the case of an odd number of electrons, *i.e.* $N = 2L + 1$ with $L \in \mathbb{N}$, we would, as illustrated in the right panel of Fig. 6.1, most naturally choose to put the extra electron in an additional orbital φ_L with either spin $\sigma = +1/2$ or spin $\sigma = -1/2$ (this latter choice concerning the spin does not really matter). This then yields the Hartree-Fock equations

$$\begin{aligned}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}^2} + V(\mathbf{r}) + 2\sum_{l'=0}^{L-1}\int d^3r' U(\mathbf{r}-\mathbf{r}')|\varphi_{l'}(\mathbf{r}')|^2\right)\varphi_l(\mathbf{r}) \\ - \sum_{l'=0}^{L-1}\int d^3r' U(\mathbf{r}-\mathbf{r}')\varphi_{l'}(\mathbf{r})\varphi^*_{l'}(\mathbf{r}')\varphi_l(\mathbf{r}') \\ + \int d^3r' U(\mathbf{r}-\mathbf{r}')\left[|\varphi_L(\mathbf{r}')|^2\varphi_l(\mathbf{r}) - \varphi_L(\mathbf{r})\varphi^*_L(\mathbf{r}')\varphi_l(\mathbf{r}')\right] &= \epsilon_l\varphi_l(\mathbf{r})\end{aligned} \tag{6.38}$$

to be solved for $l = 0, \ldots, L$ in a self-consistent manner. Note that the third line of the left-hand side of Eq. (6.38) vanishes in the special case $l = L$, which clearly accounts for the fact that the extra electron in the orbital φ_L does not electrostatically interact with itself.

It should be noted that the single-particle orbitals φ_l and their associated energy levels ϵ_l do not have a physical meaning in the strict sense, as they are obtained within the framework of an approximation. However, the picture that is suggested by Fig. 6.1, namely that two electrons with opposite spin occupy a single-particle orbital that is not too different from the corresponding eigenfunction of the one-body Hamiltonian in the non-interacting case, nevertheless represents a convenient visualization of the basic structure of the many-body ground state, which becomes closer to reality the more electrons are involved.

Providing this approximate picture is indeed a major asset of the Hartree-Fock approach. From the numerical point of view, other methods resulting from the density functional theory (which is also based on the variational principle) are nowadays more commonly used in order to provide a quantitative desription of the ground state of an electronic many-body system.