Chapter 10

Many–particle systems

In previous chapters we mostly considered the behaviour of a single quantum particle in a classical environment. We now turn to systems with many quantum particles, like electrons in solid matter or in atoms with $Z \gg 1$. The basic principle that identical particles cannot be distinguished in the quantum world will have important and far-reaching consequences.

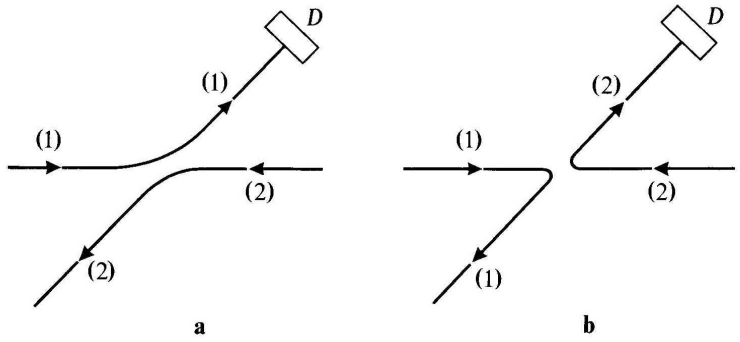

Figure 10.1: Two types of paths that the system of two colliding particles could have followed.

As an example we consider the scattering of two identical particles, as shown in figure 10.1. Oppositely polarized electrons essentially remain distinguishable because the magnetic spin interaction is negligible as compared to the electric repulsion. If the detector D counts electrons of any spin then the classical probabilities for both processes just add up

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 + |f(\pi - \theta)|^2. \tag{10.1}$$

If beams (1) and (2) are both polarized spin up then the detector cannot distinguish between the incident particles and we will see that the rules of quantum mechanics tell us to superimpose amplitudes rather than probabilities. Particles with integral spin, like α-particles, follow the Bose–Einstein statistics, which means that their amplitudes have to be added

$$\left(\tfrac{d\sigma}{d\Omega}\right)_{BE} = |f(\theta) + f(\pi - \theta)|^2, \tag{10.2}$$

while particles with half-integral spin, like electrons, obey Fermi–Dirac statistics, which means that their amplitudes have to be subtracted

$$\left(\tfrac{d\sigma}{d\Omega}\right)_{FD} = |f(\theta) - f(\pi - \theta)|^2. \tag{10.3}$$

At an angle $\theta = \pi/2$ this implies

$$\left(\tfrac{d\sigma}{d\Omega}\right)_{BE}(\tfrac{\pi}{2}) = 4\,|f(\tfrac{\pi}{2})|^2, \qquad \left(\tfrac{d\sigma}{d\Omega}\right)_{FD}(\tfrac{\pi}{2}) = 0 \tag{10.4}$$

so that identical fermions never scatter at an angle of $\pi/2$, while the differential cross section for boson scattering becomes twice the classical value for this angle [Feynman].

In the present chapter we discuss the construction of many particle Hilbert spaces and their application to systems with many identical particles. As applications we discuss the derivation of (10.1–10.3) for particle scattering and the Hartree–Fock approximation for the computation of energy levels in atoms. We then introduce the occupation number representation and discuss the quantization of the radiation field, which will allow us to compute the amplitudes for electromagnetic transitions. As a last point we briefly discuss phonons and the concept of quasiparticles.

10.1 Identical particles and (anti)symmetrization

Particles are said to be identical if all their properties are exactly the same. In classical mechanics the dynamics of a system of N identical particles is described by a Hamilton function that is invariant under all $N!$ permutations $i \to \pi_i \equiv \pi(i)$ of the index set for the positions $\vec{x}_i$ and momenta $\vec{p}_i$,

$$H(\vec{x}_1, \vec{p}_1, \ldots, \vec{x}_N, \vec{p}_N) = H(\vec{x}_{\pi(1)}, \vec{p}_{\pi(1)}, \ldots, \vec{x}_{\pi(N)}, \vec{p}_{\pi(N)}), \qquad \pi \equiv \begin{pmatrix} 1 & 2 & \ldots & N \\ \pi_1 & \pi_2 & \ldots & \pi_N \end{pmatrix}. \tag{10.5}$$

The permutation group is generated by transpositions

$$\pi_{ij} = \begin{pmatrix} 1 \ldots i \ldots j \ldots N \\ 1 \ldots j \ldots i \ldots N \end{pmatrix}, \tag{10.6}$$

and the sign $(-1)^n$ of a permutation π is defined in terms of the number n modulo 2 of required transpositions,

$$\mathrm{sign}(\pi \circ \pi') = \mathrm{sign}(\pi) \cdot \mathrm{sign}(\pi'), \qquad \mathrm{sign}(\pi_{ij}) = -1. \tag{10.7}$$

Even and odd permutations have $sign_\pi = +1$ and $sign_\pi = -1$, respectively.

Although identical particles cannot be distinguished by their properties we can number them at some instant of time and identify them individually at later times by following their trajectories, as is illustrated for the example of a scattering experiment in figure 10.1. In

quantum mechanics, however, there are no well-defined trajectories and the wave functions start to overlap in the interaction region. It is hence no longer possible to tell which of the two particles went into the detector. The principle of indistinguishability of identical particles states that there is no observable that can distinguish between the state with particle 1 at position $|x_1\rangle$ and particle 2 at position $|x_2\rangle$ and the state with the positions of the particles exchanged. But then the state vectors in the Hilbert space $\mathcal{H}_2$ of two identical particles for the states with quantum numbers $|x_1, x_2\rangle_{id}$ and $|x_2, x_1\rangle_{id}$ must be the same up to a phase

$$|x_2, x_1\rangle_{id} = e^{i\rho}|x_1, x_2\rangle_{id} \tag{10.8}$$

because otherwise, for example, the projector $|x_1, x_2\rangle\langle x_1, x_2|$ could be used to find out whether the position x_1 is occupied by particle 1 or by particle 2.

In the case of N *distinguishable* particles the wave functions $\psi(\vec{x}_1, \ldots, \vec{x}_N)$ are *arbitrary* (normalizable) functions of the N positions. An N-particle state is thus in general not a product state $\varphi_{\lambda_1}(x_1) \cdot \ldots \cdot \varphi_{\lambda_N}(x_N)$ but a superposition of such states and hence an element of the tensor product

$$\psi(x_1, \ldots, x_N) \in \mathcal{H}^N \equiv \underbrace{\mathcal{H} \otimes \ldots \otimes \mathcal{H}}_{N} \tag{10.9}$$

of N copies of the 1-particle Hilbert space. The states $|\varphi_\lambda\rangle$ can be taken from an arbitrary complete orthonormal basis of $\mathcal{H}$.

Often the positions are combined with the magnetic quantum numbers describing the spin degrees of freedom (and possibly other quantum numbers) as $q_i = (\vec{x}_i, m_i)$. Permutations π of the particles correspond to unitary operations $\mathcal{P}_\pi$ in the product space

$$\mathcal{P}_\pi|q_1 \ldots q_N\rangle = |q_{\pi(1)} \ldots q_{\pi(N)}\rangle. \tag{10.10}$$

For identical particles $|q_1, q_2\rangle_{id}$ and $|q_2, q_1\rangle_{id}$ should correspond to indistinguishable states

$$|q_j, q_i\rangle_{id} = \mathcal{P}_{ij}|q_i, q_j\rangle_{id} = e^{i\rho}|q_i, q_j\rangle_{id} \in \mathcal{H}_2 \qquad \text{with} \qquad \mathcal{P}_{ij} \equiv \mathcal{P}(\pi_{ij}) \tag{10.11}$$

in the 2-particle Hilbert space $\mathcal{H}_2$. It is now usually argued that

$$\mathcal{P}_{ij}^2|q_i, q_j\rangle_{id} = e^{2i\rho}|q_i, q_j\rangle_{id} = |q_i, q_j\rangle_{id}, \tag{10.12}$$

hence

$$2\rho \in 2\pi\mathbb{Z} \qquad \Rightarrow \qquad |q_j, q_i\rangle_{id} = \mathcal{P}_{ij}|q_i, q_j\rangle_{id} = \pm|q_i, q_j\rangle_{id}, \tag{10.13}$$

because exchanging the position twice brings us back to the original state. Particles for which $|q_j, q_i\rangle_{id} = +|q_i, q_j\rangle_{id}$ are called bosons and particles for which $|q_j, q_i\rangle_{id} = -|q_i, q_j\rangle_{id}$ are called fermions. For more than two particles every permutation can be obtained as a product of transpositions and it is easy to see that N-boson states are invariant under $\mathcal{P}_\pi$ while N-fermion

states transform with a factor $\text{sign}(\pi)$.[1] Based on the axioms of relativistic quantum field theory Wolfgang Pauli (1940) proved the spin statistic theorem, which states that particles are bosons if they have integer spin $j \in \mathbb{Z}$ and fermions if they have half-integral spin $j \in \mathbb{Z} + \frac{1}{2}$.[2]

Symmetrization and antisymmetrization. For bosons and fermions the N-particle Hilbert spaces $\mathcal{H}_N^{(B)}$ and $\mathcal{H}_N^{(F)}$ can now be constructed as subspaces of the N-particle Hilbert space $\mathcal{H}^N$ of distinguishable particles. We introduce the *symmetrization* operator

$$\mathcal{S} = \frac{1}{N!} \sum_\pi P_\pi \tag{10.14}$$

and the *antisymmetrization* operator

$$\mathcal{A} = \frac{1}{N!} \sum_\pi \text{sign}(\pi) P_\pi. \tag{10.15}$$

The operators $\mathcal{S}$ and $\mathcal{A}$ are Hermitian because $(\mathcal{P}_\pi)^\dagger = \mathcal{P}_{\pi^{-1}}$ and the set of all permutations is equal to the set of all inverse permutations, for which $\text{sign}(\pi^{-1}) = \text{sign}(\pi)$. Similarly it can be shown that both operators are idempotent

$$\mathcal{S}^2 = \frac{1}{N!} \sum_\pi P_\pi \mathcal{S} = \frac{1}{N!} \sum_\pi \mathcal{S} = \mathcal{S} = \mathcal{S}^\dagger, \tag{10.16}$$

$$\mathcal{A}^2 = \frac{1}{N!} \sum_\pi \text{sign}(\pi) P_\pi \mathcal{A} = \frac{1}{N!} \sum_\pi \mathcal{A} = \mathcal{A} = \mathcal{A}^\dagger \tag{10.17}$$

and hence projection operators. States of the form $\mathcal{S}|\psi\rangle$ and $\mathcal{A}|\psi\rangle$ are eigenstates of the transposition operator $\mathcal{P}_{ij}$ with eigenvalues $+1$ and -1, respectively. Moreover, $\mathcal{S}$ and $\mathcal{A}$ project onto orthogonal eigenspaces, $\mathcal{S}\mathcal{A} = \mathcal{A}\mathcal{S} = 0$, and commute with all observables $\mathcal{O}$ for identical particles

$$[\mathcal{S}, \mathcal{O}] = [\mathcal{A}, \mathcal{O}] = 0 \tag{10.18}$$

because such observables must be invariant under every exchange of two identical particles $[\mathcal{P}_{ij}, \mathcal{O}] = 0$. The images of the projectors $\mathcal{S}$ and $\mathcal{A}$ hence can be used as Hilbert spaces for the

[1] The conclusion $\mathcal{P}_{ij}^2 = \mathbb{1}$ in eq. (10.12) is not stringent because, in principle, $\mathcal{P}_{ij}^2$ could differ from the identity by a phase. For 2-dimensional quantum systems that violate parity it is indeed conceivable that the phase $e^{i\rho}$ in (10.11) depends on the direction in which the particles are moved about one another so that the phase of $\mathcal{P}_{ij} = \mathcal{P}_{ji}^{-1}$ remains free. The particles are then neither bosons nor fermions and were therefore called *anyons* in the 1970s. For rational phases $\frac{1}{2\pi}\rho \in \mathbb{Q}$ such particles would have *fractional statistics* or *braid group statistics*. In the present context the braid group relates to the permutation group in the same way as the spin group $SU(2)$ relates to the rotation group $SO(3)$: A double exchange, like a rotation by 2π, is physically unobservable but still can lead to a non-trivial phase in quantum mechanics. The permutation of two particles in two dimensions can thus be regarded as a braiding process where the phase $e^{i\rho}$ depends on which strand is above and which strand is below.

Fractional statistics presumably has indeed been observed in the 1980s in the *fractional quantum Hall effect*, where charge carriers with fractional charges $Q = 1/3$ ... up to about $Q = 1/11$ have been observed. These are believed to be "quasi-particles" that obey a corresponding fractional statistics. Parity violation in these effectively two-dimensional thin layers is due to a strong magnetic field.

[2] In two dimensions the rotation group $SO(2)$ is abelian and therefore spin is not quantized. In accord with the spin-statistics connection fractional statistics, as discussed in the previous footnote, comes along with fractional spin of the quasi-particles on the fractional quantum Hall effect.

quantum mechanical description of identical particles

$$\mathcal{H}_N^{(B)} = \mathcal{S}(\underbrace{\mathcal{H}\otimes\ldots\otimes\mathcal{H}}_{N}), \qquad \mathcal{H}_N^{(F)} = \mathcal{A}(\underbrace{\mathcal{H}\otimes\ldots\otimes\mathcal{H}}_{N}). \tag{10.19}$$

Operators corresponding to permutation invariant observables automatically restrict to well-defined operators on $\mathcal{H}_N^{(B)}$ and on $\mathcal{H}_N^{(F)}$.

Given some basis $|q_j\rangle$ of $\mathcal{H}$ we now want to construct useful bases for the Hilbert spaces $\mathcal{H}_N$ of N identical particles. To get started we consider the examples of antisymmetrized two-particle and three-particle states

$$|q_1,q_2\rangle_A = \tfrac{1}{\sqrt{2}}(|q_1\rangle\otimes|q_2\rangle - |q_2\rangle\otimes|q_1\rangle) = \sqrt{2}\,\mathcal{A}|q_1,q_2\rangle, \tag{10.20}$$

$$|q_1,q_2,q_3\rangle_A = \tfrac{1}{\sqrt{3!}}\sum_\pi \mathrm{sign}(\pi)\,|q_{\pi_1}\rangle^{(1)}\,|q_{\pi_2}\rangle^{(2)}\,|q_{\pi_3}\rangle^{(3)} = \sqrt{3!}\,\mathcal{A}|q_1,q_2,q_3\rangle, \tag{10.21}$$

where the superscript i of $|q_j\rangle^{(i)}$ refers to the number of the particle and the subscript j refers to the quantum numbers labelling an orthonormal basis of 1-particle wave functions $\varphi_j(\vec{x}) \equiv |q_j\rangle \in \mathcal{H}$. It is easily verfied that ${}_A\langle q_1,q_2|q_1,q_2\rangle_A = {}_A\langle q_1,q_2,q_3|q_1,q_2,q_3\rangle_A = 1$. More generally, the antisymmetrized product states

$$|q_1,q_2,\ldots\rangle_A = \sqrt{N!}\,\mathcal{A}|q_1,q_2,\ldots\rangle \tag{10.22}$$

provide an orthonormal basis of $\mathcal{H}_N^{(F)}$,

$${}_A\langle q_1,q_2,\ldots|q_1,q_2,\ldots\rangle_A = 1, \qquad q_i \neq q_j \quad \text{for} \quad i\neq j, \tag{10.23}$$

where the normalization factor had to be chosen as $\sqrt{N!}$ because only the $N!$ scalar products in the double sum over all permutations of the *bra* and the *ket* vectors for which the permutations match contribute to the norm. The antisymmetrization of a product state can also be written as a determinant

$$\psi_A(q_1,\ldots,q_N) = \sqrt{N!}\,\mathcal{A}\,|q_1,\ldots,q_N\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix} |q_1\rangle^{(1)} & |q_1\rangle^{(2)} & \ldots & |q_1\rangle^{(N)} \\ \vdots & \vdots & & \vdots \\ |q_N\rangle^{(1)} & |q_N\rangle^{(2)} & \ldots & |q_N\rangle^{(N)} \end{vmatrix}, \tag{10.24}$$

called *Slater determinant*, which vanishes if two quantum numbers agree. Antisymmetrization hence implies Pauli's exclusion principle.

For bosons we can similarly construct an orthonormal basis as

$$|q_1\ldots q_N\rangle_S = \sqrt{\frac{N!}{n_1!\ldots n_r!}}\,\mathcal{S}|q_1\ldots q_N\rangle, \qquad \sum_{j=1}^{r} n_j = N, \tag{10.25}$$

where the normalization ${}_S\langle q_1\ldots q_N|q_1\ldots q_N\rangle_S = 1$ has required additional factors $1/\sqrt{n_j!}$ if groups of n_j of the quantum numbers q_i agree because then all terms where the order of identical

quantum numbers is exchanged also contribute in the double sum over all permutations of the quantum numbers of the *bra* and the *ket* vectors. (If, for example, all quantum numbers agree, then $|q,\ldots,q\rangle$ is already symmetric and the prefactor becomes $\sqrt{N!/N!}=1$). In analogy to the Slater determinant the symmetrization of product states is sometimes written in terms of the *permutant* $\left|\,|q_i\rangle^{(j)}\right|_+$,

$$\mathcal{S}\,|q_1,\ldots,q_N\rangle = \frac{1}{N!}\begin{vmatrix} |q_1\rangle^{(1)} & |q_1\rangle^{(2)} & \ldots & |q_1\rangle^{(N)} \\ \vdots & \vdots & & \vdots \\ |q_N\rangle^{(1)} & |q_N\rangle^{(2)} & \ldots & |q_N\rangle^{(N)} \end{vmatrix}_+ , \tag{10.26}$$

which is defined similarly to the determinant except that all signs of the $N!$ terms are positive.

10.2 Electron-electron scattering

The above considerations imply that our ansatz (8.20) for the asymptotic scattering wave function

$$u_{as} = (e^{i\vec{k}\cdot\vec{x}})_{as} + f(k,\theta)\frac{e^{ikr}}{r} \tag{10.27}$$

has to be modified for identical particles. With $u_S=\sqrt{2}\mathcal{S}u_{as}$ and $u_A=\sqrt{2}\mathcal{A}u_{as}$ it becomes

$$u_{\{_A^S} = \frac{1}{\sqrt{2}}\left((e^{i\vec{k}\vec{x}}\pm e^{-i\vec{k}\vec{x}}) + (f(\theta)\pm f(\pi-\theta))\frac{e^{ikr}}{r} + \mathcal{O}(\frac{1}{r^2})\right) \tag{10.28}$$

in the center of mass system, which leads to the differential cross section

$$\frac{d\sigma}{d\Omega} = |f(\theta)\pm f(\pi-\theta)|^2 \tag{10.29}$$

as we anticipated in the introduction of the present chapter.

For non-scalar wave functions we have to be more precise, however, because antisymmetrization non only affects the positions but also the other quantum numbers. For scattering of identical spin 1/2 particles like electrons the relevant quantum numbers are the relative coordinate $\vec{x}$ and the magnetic quantum numbers m_1, m_2 of the two particles. In the total spin basis the spin part of the wave function is either in the singlet state

$$|u\rangle^{(singlet)} = u_S(\vec{x})\chi_S, \qquad \chi_S = \tfrac{1}{\sqrt{2}}(\,|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \tag{10.30}$$

or in the triplet state

$$|u\rangle^{(triplet)} = u_T(\vec{x})\chi_T, \qquad \chi_T = \begin{cases} |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}}(\,|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\downarrow\downarrow\rangle \end{cases}. \tag{10.31}$$

Since the spin part of the singlet is antisymmetric the total antisymmetrization leads to a symmetrization of the position space wave function and hence

$$\left(\frac{d\sigma}{d\Omega}\right)_S = |f(\theta)+f(\pi-\theta)|^2\,, \tag{10.32}$$

while the triplet is symmetric under exchange of the two electrons so that the position part has to be antisymmetrized

$$\left(\frac{d\sigma}{d\Omega}\right)_T = |f(\theta) - f(\pi-\theta)|^2 \,. \tag{10.33}$$

For unpolarized electrons the triplet state is 3 times more likely than the singlet state and since

$$|f(\theta) \pm f(\pi-\theta)|^2 = |f(\theta)|^2 + |f(\pi-\theta)|^2 \pm \Big(f(\theta)f^*(\pi-\theta) + f^*(\theta)f(\pi-\theta)\Big) \tag{10.34}$$

the classical probabilities $\rho_T = 3/4$ and $\rho_T = 1/4$ imply

$$\frac{d\sigma}{d\Omega} = \frac{3}{4}\left(\frac{d\sigma}{d\Omega}\right)_T + \frac{1}{4}\left(\frac{d\sigma}{d\Omega}\right)_S = |f(\theta)|^2| + f(\pi-\theta)|^2 - \mathrm{Re}\Big(f(\theta)f^*(\pi-\theta)\Big)\,. \tag{10.35}$$

This is in accord with our anticipation that electrons with different spin orientation experience no quantum interference while the exclusion principle affects the 50% of the scattering events where both spins are up or both spins are down.

For Coulomb scattering of electrons we recall formula (8.145) for the amplitude,

$$f(\theta) = -\frac{\gamma}{2k\sin^2(\theta/2)} e^{i(2\sigma_0 - \gamma\log\sin^2(\theta/2)} \tag{10.36}$$

with $\sigma_0 = \mathrm{Im}\log\Gamma(1+i\gamma)$, and hence

$$f(\pi-\theta) = -\frac{\gamma}{2k\cos^2(\theta/2)} e^{i(2\sigma_0 - \gamma\log\cos^2(\theta/2)}. \tag{10.37}$$

In $f(\theta)f^*(\pi-\theta)$ the constant σ_0 drops out and the logarithms combine to $\log\tan^2(\theta/2)$. We thus arrive at *Mott's scattering formula*

$$\frac{d\sigma}{d\Omega} = \frac{\gamma^2}{4k^2}\left(\frac{1}{\sin^4(\theta/2)} + \frac{1}{\cos^4(\theta/2)} - \frac{\cos(\gamma\log\tan^2(\theta/2))}{\sin^2(\theta/2)\cos^2(\theta/2)}\right), \tag{10.38}$$

which shows that the quantum mechanical interference term and its modification by the phase correction to the classical formula for Coulomb scattering can be observed already for unpolarized electrons.

10.3 Selfconsistent fields and Hartree-Fock

The Hamilton function for an atom with N electrons and nuclear charge Z consists of the kinetic and potentials energies $T_i + V_i$ of the electrons in the electric field of the nucleus and the repulsive interaction terms W_{ij} among the electrons,

$$H \;=\; \sum_{i=1}^{N}(T_i + V_i) + \frac{1}{2}\sum_{i\neq j} W_{ij} \;=\; \sum_{i=1}^{N}\left(\frac{\vec{p}_i{}^2}{2m} - \frac{Ze^2}{r_i}\right) + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{x}_i - \vec{x}_j|} \tag{10.39}$$

or

$$H \;=\; H^{(1)} + H^{(2)} \qquad \text{with} \qquad H^{(1)} = \sum_{i=1}^{N} (T_i + V_i), \quad H^{(2)} = \frac{1}{2} \sum_{i \neq j} W_{ij}. \tag{10.40}$$

If N is large then it is plausible to assume that the potential that is felt by an individual electron is approximately independent of its own motion. We can hence think of each electron as moving in a *mean field* that is determined a posteriory in a *self consistent* way, i.e. we compute the electron states for a given potential $\widetilde{V}_i$ and then make sure that the electron states indeed produce exactly (or at least approximately) that potential.

In the present section we discuss selfconsistent methods for a *central potential* $V(r)$, i.e. in the context of atomic physics. Similar methods can also be used for solids, where the electrons move in the periodic potential of the nuclei that are located on a crystal lattice.

The Hartree method. Under the assumptions of the selfconsistent approach we can determine energy eigenstates $|\varphi_\alpha(\vec{x})\rangle$ by solving the Schrödinger equation for $\tilde{H}_i = T_i + \tilde{V}_i$ and then fill up the available orbits with increasing energies. This is motivation for the Hartree approximation, which assumes that the wave functiton is of the product form

$$\psi(q_1, \ldots, q_N) = \varphi_{\alpha_1}(q_1) \ldots \varphi_{\alpha_N}(q_N) \tag{10.41}$$

where $\varphi_i(q_i) = \varphi_i(\vec{x}_i)\chi_i$ are energy eigenstates

$$\tilde{H}_i|\varphi_i\rangle = (T_i + \tilde{V}_i)|\varphi_i\rangle = E_i|\varphi_i\rangle \tag{10.42}$$

and $\chi_i = |\frac{1}{2}, \pm\frac{1}{2}\rangle$ describes the spin degree of freedom. Within this class of wave fuctions the φ_i are determined with the help of the variational principle. The Pauli exclusion principle is implemented in the naiv way of assuming that any two eigenfunctions $\varphi_{\alpha_i}(\vec{x})$ and $\varphi_{\alpha_j}(\vec{x})$ are different except for a possible two-fold degeneracy for electrons that differ by their spin degrees of freedom $\chi_i \neq \chi_j$.

The variational method has been introduced in chapter 6, where we have shown that the Schrödinger equation is equivalent to the variational equation $\delta E[\psi] = 0$ for the energy functional $E[\psi] = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$, which assumes its minimum exactly if ψ is the ground state wave function. If ψ is restricted to belong to a family of trial wave functions then an approximation to the ground state is obtained by minimizing $E[\psi]$ within that family. The quality of this approximation depends on the quality of chosen candidate family. In the Hartree approximation the family consists of all N-particle wave functions of the product form (10.41).

The main trick of this approach is to implement the orthonormalization of the one-particle wave functions φ_i by a collection of Lagrange multipliers ε_{ij}. We hence extremize the extended functional

$$E[\psi, \varepsilon_{ij}] = \langle\psi|H\psi\rangle + \sum_{i,j} \varepsilon_{ij} \Big(\delta_{ij} - \langle\varphi_i|\varphi_j\rangle\Big) \tag{10.43}$$

for arbitrary variations of $|\varphi_i\rangle$ and ε_{ij}. In order to simplify out notation we ignore for a moment a possibe degeneracy of the configuration space wave functions $\varphi_{\alpha_i}(\vec{x}) = \varphi_{\alpha_j}(\vec{x})$ in case of different spins $s_i \neq s_j$, which would reduce the number of Lagrange multipliers. For the evaluation of the expectation value $\langle\psi|H\psi\rangle$ it is important to note that the one-particle part $H^{(1)}$ of the Hamiltonian (10.39) is a sum of terms that only act on one of the factors of the product wave function (10.41) while all others are unaffected so that the respective *bra*'s and *ket*'s multiply to 1,

$$\langle\psi|\ H^{(1)}\ |\psi\rangle = \sum_{i=1}^{N} \langle\varphi_i|\ (T_i + V_i)\ |\varphi_i\rangle. \tag{10.44}$$

Similarly, the two-particle Hamiltonian $H^{(2)}$, which describes the interaction of two electrons, consists of a sum of terms that only act on two factors of the wave function, while the remaining factors can again be ignored,

$$\langle\psi|\ H^{(2)}\ |\psi\rangle = \frac{1}{2}\sum_{i\neq j} \langle\varphi_i, \varphi_j|\ W_{ij}\ |\varphi_i, \varphi_j\rangle. \tag{10.45}$$

Since orthonormality of the $|\varphi_i\rangle$ is implemented by the Lagrange multipliers we can freely vary all factors $\varphi_i(x_i)$ of the wave function $|\psi\rangle$. In the treatment of the variational method in chapter 6 we have shown that extremality under real and imaginary variations of $\varphi_i(\vec{x}_i)$ is equivalent to a formally independent variation of the bra-vector $\langle\delta\varphi_i|$ with fixed ket $|\varphi_i\rangle$. The variational equation hence becomes

$$\begin{aligned}\delta E[\psi, \varepsilon_{ij}] \;=\; & \sum_{i=1}^{N}\langle\delta\varphi_i|(T_i + V_i)|\varphi_i\rangle + \frac{1}{2}\sum_{i\neq j}\ \Big(\langle\delta\varphi_i, \varphi_j| + \langle\varphi_i, \delta\varphi_j|\Big)\ W_{ij}\ |\varphi_i, \varphi_j\rangle \\ & - \sum_{ij}\langle\delta\varphi_i|\varepsilon_{ij}|\varphi_j\rangle = 0\end{aligned} \tag{10.46}$$

which implies

$$(T_i + V_i)|\varphi_i\rangle + \sum_{j\neq i}\langle\varphi_j|W_{ij}|\varphi_j\rangle\,|\varphi_i\rangle = \sum_j \varepsilon_{ij}|\varphi_j\rangle. \tag{10.47}$$

Since the Lagrange multipliers ε_{ij} in (10.43) form a Hermitian matrix this matrix can be diagonalized by a unitary transformation of the $|\varphi_i\rangle$. We thus obtain the *Hartree equation*, which can be written in a more explicit notation as

$$\left(-\frac{\hbar^2}{2m}\Delta - \frac{Ze^2}{r}\right)\varphi_i(\vec{x}) + e^2\sum_{j\neq i}\int\frac{|\varphi_j(\vec{x}\,')|^2}{|\vec{x} - \vec{x}\,'|}d^3x'\ \varphi_i(\vec{x}) = \varepsilon_i|\varphi_i\rangle. \tag{10.48}$$

In addition to the one-particle potential V_i it contains the *Hartree potential*

$$V_i^H(\vec{x}) = \langle\varphi_j|W_{ij}|\varphi_j\rangle = e^2\sum_{j\neq i}\int\frac{|\varphi_j(\vec{x}')|^2}{|\vec{x} - \vec{x}'|}d^3x', \tag{10.49}$$

which describes the combined repulsion by the other electrons. The entries ε_i of the diagonalized matrix of Lagrange multipliers thus obtain the meaning of energy eigenvalues of an auxiliary

one-particle Schrödinger equation (10.42) with potential $\widetilde{V}_i = V_i + V_i^H$. The complete binding energy of the system can now be written as

$$E = \langle H \rangle = \sum_{i=1}^{N} \varepsilon_i - \frac{e^2}{2} \sum_{i \neq j} \iint |\varphi_i(\vec{x})|^2 \frac{1}{|\vec{x} - \vec{x}'|} |\varphi_j(\vec{x}')|^2 \, d^3x d^3x', \tag{10.50}$$

where the energy of the electron-electron interaction has to be subtracted because is counted twice in the sum over the one-particle energies ε_i.

Hartree–Fock. We now improve the product ansatz for the wave function by antisymmetrization, as we should for fermionic N-particle states, and replace (10.41) by

$$\psi_A(q_1, \ldots, q_N) = \sqrt{N!}\, \mathcal{A}\, \varphi_{\alpha_1}(q_1) \ldots \varphi_{\alpha_N}(q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(q_1) & \ldots & \varphi_{\alpha_1}(q_N) \\ \vdots & & \vdots \\ \varphi_{\alpha_N}(q_1) & \ldots & \varphi_{\alpha_N}(q_N) \end{vmatrix}. \tag{10.51}$$

Evaluating the functional (10.43) for the Hartree–Fock family $\{\psi_A\}$ of wave fuctions it is straightforward to verify that the expectation value of the one-particle Hamiltonian $H^{(1)}$ remains unchanged, while the two-particle interaction term (10.45) obtains an additional contribution,

$$\langle \psi_A |\, H^{(2)} \, | \psi_A \rangle = \frac{1}{2} \sum_{i \neq j} \Big(\langle \varphi_i, \varphi_j |\, W_{ij} \, | \varphi_i, \varphi_j \rangle - \langle \varphi_j, \varphi_i |\, W_{ij} \, | \varphi_i, \varphi_j \rangle \Big), \tag{10.52}$$

because now also permutations for which the two interacting particles are exchanged can have a non-vanishing expectation value. The detailed calculation can be done by cancelling the normalization factor $(1/\sqrt{N!})^2$ of the Stater determinants against the sum over all permutations of the positions in the *ket*-vectors. This leaves us with a signed sum over all orderings of the *bra* quantum numbers for a fixed *ket*. But then the contribution of nontrivial permutations of the *bra* vectors vanishes because of the orthogonality of the factors of ψ unless all displaced factors are modified by the action of a nontrivial operator. For the two-particle operator W_{ij} this keeps the identity and the transposition $\mathcal{P}_{ij}$. For the one-particle operator $H^{(1)}$ only the trivial permutation survives.

The second term in (10.52) is called *exchange energy*. Since it is negative it amounts to an attractive force that reduces the mutual repulsion of the electron. Variation of the *bra*-vectors in (10.52) adds an exchange contribution

$$- \sum_{i \neq j} \langle \varphi_j, \delta\varphi_i |\, W_{ij} \, | \varphi_i, \varphi_j \rangle \tag{10.53}$$

to the variational equation and we obtain the *Hartree–Fock equation*

$$\boxed{T_i|\varphi_i\rangle + V_i|\varphi_i\rangle + \sum_{j \neq i} (\langle \varphi_j | W_{ij} | \varphi_j \rangle) | \varphi_i \rangle - \sum_{j \neq i} (\langle \varphi_j | W_{ij} | \varphi_i \rangle) | \varphi_j \rangle = \varepsilon_i |\varphi_i\rangle,} \tag{10.54}$$

which is an integro-differential equation for $\varphi_i(x)$ because T_i acts as a differential operator while $\varphi_i(x')$ is integrated over in the exchage term. Including the spin degrees of freedom into our discussion we note that the sum over $j \neq i$ in the exchange terms is restricted to equal spins because the product $\langle\varphi_j|W_{ij}|\varphi_i\rangle$ is proportional to $\delta_{s_i s_j}$. This is in accord with our experience from electron scattering, where quantum interference also occured only for equal spin directions. The expectation value of the total energy for the Hartree–Fock wave function thus becomes

$$\begin{aligned}\langle\psi_A|H|\psi_A\rangle &= \sum_{i=1}^{N}\langle\varphi_i|(T_i+V_i)|\varphi_i\rangle + \frac{e^2}{2}\sum_{i\neq j}\iint |\varphi_i(\vec{x})|^2\frac{1}{|\vec{x}-\vec{x}\,'|}|\varphi_j(\vec{x}\,')|^2\, d^3x d^3x' \\ &\qquad -\frac{e^2}{2}\sum_{i\neq j}\delta_{s_i s_j}\iint \frac{\varphi_i^*(\vec{x})\varphi_j(\vec{x})\;\varphi_j^*(\vec{x}\,')\varphi_i(\vec{x}\,')}{|\vec{x}-\vec{x}\,'|}\, d^3x d^3x' \qquad (10.55)\\ &= \sum_{i=1}^{N}\varepsilon_i - \frac{e^2}{2}\sum_{i\neq j}\iint |\varphi_i(\vec{x})|^2\frac{1}{|\vec{x}-\vec{x}\,'|}|\varphi_j(\vec{x}\,')|^2\, d^3x d^3x' \\ &\qquad +\frac{e^2}{2}\sum_{i\neq j}\delta_{s_i s_j}\iint \frac{\varphi_i^*(\vec{x})\varphi_j(\vec{x})\;\varphi_j^*(\vec{x}\,')\varphi_i(\vec{x}\,')}{|\vec{x}-\vec{x}\,'|}\, d^3x d^3x'. \qquad (10.56)\end{aligned}$$

for solutions to the Hartree–Fock equation.

Summarizing, the Hartree–Fock approximation is a variational procedure so that the result can only be as close to the correct ground state wave fuction as one can get with an antisymmetrized product wave function in the much larger N-particle Hilbert space $\mathcal{H}_N$. On top of this, the Hartree–Fock equation (10.54) can only be solved approximately, which is usually done by a numerical interation. A resonable starting point for this interation can be constructed by following the semiclassical ideas of L.H. Thomas (1926) and E. Fermi (1928).

The Thomas–Fermi method. This method is based on the idea that the uncertainty principle implies that each particle occupies at least a volume $d^3x d^3p \approx \hbar^3$ in phase space. According to Pauli's exclusion principle N electrons hence occupy a volume of at least $\hbar^3\, N/2$ where the factor $1/2$ accounts for the two allowed spin projections. For a classical Hamilton function $H(\vec{x},\vec{p}) = \frac{\vec{p}^2}{2m} + V(\vec{x})$ we can then assume that the density of states $f(\vec{x},\vec{p})$ in phase space has the constant value $2/\hbar^3$ up to the energy level E_F that is required for accomodating N particles and vanishes for higher energies $H(\vec{x},\vec{p}) > E_F$. This energy level is refered to as *Fermi surface* because if bounds the volume in phase space that is occupied by the N particles. The momentum $p_F(r) = \sqrt{2m(E_F - V(r))}$ is called *Fermi momentum*, which obviously is position dependent. These ideas have a wide range of application including nuclear physics and an easy derivation of an estimate for the size of neutron stars.

Density functional theory. Modern computations in chemistry and in solid state physics are mostly based on this improvement of the Hartree–Fock method, which is based on the theorem of P. Hohenberg and W. Kohn theorem (1964) stating that the ground state energy can

be expressed as a functional $E[\rho]$ of the electron density $\rho(\vec{x})$. This functional is a sum of the Hartree energy $H_{Hartree}$, the exchange energy $H_{exchange}$ and the correlation energy $H_{correlation}$, which accounts for the fact that the correct ground state wave function is not of the anti-symmetrized product form. In less fancy terms, the correlation energy is simply all the rest. Unfortunately, the correlation functional is not known explicitly, but it is determined by the Kohn–Sham equation (1965), which serves as the analog of the Hartree equation. Popular approaches to the solution of that equation go under the names LDA (local density approximation) and LSD (local spin density approximation).

10.4 Occupation number representation

We have seen that it is often useful to describe states $|\psi\rangle \in \mathcal{H}_N$ of systems with a large number N of identical particles in terms of a basis of symmetrized or antisymmetrized products states whose factors belong to a fixed basis $|\varphi_i\rangle$ of the one-particle Hilbert space $\mathcal{H}$. Such a product state is then uniquely described by the occupation numbers n_i of the states $|\varphi_i\rangle$, where n_i counts how often the vector $|\varphi_i\rangle$ occurs as a factor in the product state. Since $N = \sum n_i$ only a finite number of occupation numbers is nonzero and for fermions n_i is restricted to the values 0 and 1. A basis vector of $\mathcal{H}_N$ can hence be simply be characterized by the collection of nonzero occupation numbers

$$|n_{i_1} \dots n_{i_L}\rangle \qquad \text{with} \qquad \textstyle\sum_{l=1}^{L} n_{i_l} = N, \tag{10.57}$$

where it is usually clear from the context whether we are talking about bosons or fermions.

The Fock space. It is now a small step to drop the condition of having a fixed particle number N. Nonconstant particle numbers are needed for many purpuses, like the description of grand canonical ensembles in statistical mechanics, particle creation in relativistic quantum field theory, but also for the description of photons or phonons, which can be created with little energy in quantum optics of solid state physics. The appropriate Hilbert space is now the infinite direct sum of the N-particle spaces for $N = 0, 1, 2, \dots$, which is called *Fock space*

$$\mathcal{F} = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \mathcal{H}_2 \oplus \mathcal{H}_3 \oplus \dots \tag{10.58}$$

where $\mathcal{H}_1 = \mathcal{H}$ and $\mathcal{H}_0$ is the 0-dimensional Hilbert space $\mathbb{C}$. In a sense, the bosonic Fock space $\mathcal{F}^{(B)}$ is much larger than the fermion one $\mathcal{F}^{(F)}$, because the occupation numbers are not restricted to $n_{i_l} \leq 1$.[3]

Creation and annihilation operators. All operators that we inherited from the single-particle Hilbert space can change occupation numbers but do not change N. Once we have introduced the Fock space we should also consider operators that allow us to change the total

[3]One the other hand, they are of equal size in the sense that both remain seperable if $\mathcal{H}$ is separable.

number of particles. We first discuss the case of bosons. In order to increase a particular occupation number n_i by one we tensor with $\sqrt{N+1}\,|\varphi_i\rangle$ and symmetrize. The resulting map from $\mathcal{H}_N^{(B)}$ to $\mathcal{H}_{N+1}^{(B)}$ is called creation operator $a_i^\dagger$ and it acts as

$$a_i^\dagger\,|n_{i_1}\dots n_i\dots n_{i_L}\rangle = \sqrt{N+1}\,\mathcal{S}(|\varphi_i\rangle\otimes|n_{i_1}\dots n_i\dots n_{i_L}\rangle) \tag{10.59}$$

$$= \sqrt{n_i+1}\,|n_{i_1}\dots(n_i+1)\dots n_{i_L}\rangle \tag{10.60}$$

on the normalized basis vectors, where the factor $\sqrt{n_i+1}$ in the second line follows from

$$\mathcal{S}\left(|q_0\rangle\otimes\sqrt{\tfrac{N!}{\prod n_i!}}\,\mathcal{S}\,|q_1\dots q_N\rangle\right) = \sum_1^{(N+1)!}\tfrac{\mathcal{P}_\pi}{(N+1)!}\sqrt{\tfrac{N!}{\prod n_i!}}\sum_1^{N!}\tfrac{\mathcal{P}_{\pi'}}{N!}|q_0q_1\dots q_N\rangle \tag{10.61}$$

$$= \sqrt{\tfrac{N!}{\prod n_i!}}\sum_1^{(N+1)!}\tfrac{\mathcal{P}_\pi}{(N+1)!}|q_0q_1\dots q_N\rangle = \sqrt{\tfrac{n_i+1}{N+1}}\,|q_0q_1\dots q_N\rangle_S \tag{10.62}$$

in the notation of formula (10.25). The adjoint of the creation operator in Fock space is called annihilation operator and its action on the basis vectors is

$$a_i\,|n_{i_1}\dots n_i\dots n_{i_L}\rangle = \sqrt{n_i}\,|n_{i_1}\dots(n_i-1)\dots n_{i_L}\rangle. \tag{10.63}$$

With (10.60) and (10.63) it is now easily verified that creation operators $a_i^\dagger$ and annihilation operators a_j commute for $i\neq j$, while they satisfy the same algebraic relations as those of the harmonic oscillator if $i=j$. All commutation relations are summarized in the formulas

$$\boxed{[a_i,a_j]=0,\qquad [a_i,a_j^\dagger]=\delta_{ij},\qquad [a_i^\dagger,a_j^\dagger]=0.} \tag{10.64}$$

Some authors use b_i for bosonic and a_i for fermionic annihilation operators but we prefer to keep the a of the harmonic oscillator for the bosonic case.

Fermions. The same construction can now be applied to fermions. Since now all nonzero occupation numbers are 1 we can drop the redunant n from the notation and denote the states by $|i_1\dots i_L\rangle$. Accordingly the normalizations simplify. But on the other hand orderings and signs have to be treated more carefully because the sign of a state changes for every transposition,

$$|i_1\dots i_k\dots i_l\dots i_L\rangle = -|i_1\dots i_l\dots i_k\dots i_L\rangle. \tag{10.65}$$

The fermionic creation operators $b_i^\dagger$ are again defined by tensoring with $\sqrt{N+1}\,|\varphi_i\rangle$, but now with a subsequent antisymmetrization so that we obtain

$$b_i\,|ii_1i_2\dots i_L\rangle = |i_1i_2\dots i_L\rangle,\qquad b_i^\dagger\,|i_1i_2\dots i_L\rangle = \begin{cases}|i\,i_1i_2\dots i_L\rangle & \text{if } n_i=0\\ 0 & \text{if } n_i=1\end{cases}, \tag{10.66}$$

and b_i vanishes if $n_i=0$. For fermions the sign changes whenever we transpose two positions. We hence obtain the same algebra as for bosons, except that now all commutators are replaced by anticommutators

$$\boxed{\{b_i,b_j\}=0,\qquad \{b_i,b_j^\dagger\}=\delta_{ij},\qquad \{b_i^\dagger,b_j^\dagger\}=0.} \tag{10.67}$$

These formulas are easily verified for our basis of the Fock space by using the definitions (10.66).

Operators and occupation numbers. For bosons, as well as for fermions, every basis vector of the Fock space can now be obtained by repeated application of creation operators from the Fock vacuum $|0\rangle$, for which all occupation numbers are zero and which is hence a normalized state in $\mathcal{H}_0$. As for the harmonic oscillator we can define the occupation number operators

$$N^{(B)} = \sum_k a_k^\dagger a_k, \qquad N^{(F)} = \sum_k b_k^\dagger b_k, \tag{10.68}$$

which count the occupation numbers for bosons and fermions, respectively. It is a beautiful feature of this formalism that we can rewrite all our previous operators for identical particles in terms of creation and annihilation operators [Hittmair]. For a single-particle operator like $V = \sum_{i=1}^N V(x_i)$ the formula is

$$V = \sum_{ij} \langle i|V|j\rangle \; a_i^\dagger a_j. \tag{10.69}$$

For two-particle operators like the electron-electon interaction $W = \frac{1}{2}\sum_{i\neq j} W_{ij}$ one can show that

$$W = \frac{1}{2}\sum_{ijkl} \langle ij|W|kl\rangle \; a_i^\dagger a_j^\dagger a_l a_k. \tag{10.70}$$

An important special case of this is the Hamilton operator of non-interacting particles, which is a one-particle operator so that

$$H^{(1)} = \sum_i \hbar\omega_i \; a_i^\dagger a_i \tag{10.71}$$

where $H|\varphi_i\rangle = \hbar\omega_i|\varphi_i\rangle$. From the analogy with the harmonic oscillator we expect an additional contribution from the zero point energies. A constant is, however, not a one-particle but rather a zero-particle operator, whose contribution could be recovered as $H^{(0)} = \langle 0|H|0\rangle$. In any case, a constant contribution to the Hamilton function is unobservable in quantum mechanics.

10.4.1 Quantization of the radiation field

Our first application of the occupation number formalism is the quantization of the electromagnetic field in an intuitive and simplified form where we are only interested in radiation and exclude Coulomb interactions. In the *absence of charges* the Maxwell equations for the electromagnetic potentials are

$$\Box A_\mu - \partial_\mu \partial_\nu A^\nu = 0. \tag{10.72}$$

Imposing the *Coulomb gauge*

$$\nabla \vec{A}(\vec{x}, t) = 0 \tag{10.73}$$

the equation for the scalar potential $\phi = A^0$ becomes

$$\Box\,\phi - \frac{1}{c^2}\partial_t^2\phi \;=\; -\Delta\phi \;=\; 0, \tag{10.74}$$

which contains no time derivative so that ϕ is not dynamical and can be set to $\phi = 0$. This gauge is also called *radiation gauge* and the vector potential equation becomes

$$\Box\vec{A}(\vec{x},t) = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{A}(\vec{x},t) - \Delta\vec{A}(\vec{x},t) = 0 \tag{10.75}$$

with

$$\vec{E}(\vec{x},t) = -\frac{1}{c}\frac{\partial}{\partial t}\vec{A}(\vec{x},t), \qquad \vec{B}(\vec{x},t) = \nabla\times\vec{A}(\vec{x},t). \tag{10.76}$$

Its solutions $\vec{A}(\vec{x},t)$ can be written as superpositions of plane waves $e^{i(\vec{k}\vec{x}-\omega t)}$ with $\omega = c\,|\vec{k}|$.

To simplify the subsequent discussion we put our system into a large box with volume $V = L^3$ and impose periodic boundary conditions (physical boundary conditions would be inconsistent with $\phi = 0$ because of the presence of surface charges). For later convenience the coefficients in the Fourier series of the vector potential $\vec{A}(\vec{x},t)$ are normalized such that

$$\vec{A}(\vec{x},t) = \sum_{\vec{n}\in\mathbb{Z}^3}\sqrt{\tfrac{2\pi\hbar c^2}{L^3\omega}}\left(\vec{a}_k\; e^{i(\vec{k}\vec{x}-\omega t)} + \vec{a}_k^{\,*}\; e^{-i(\vec{k}\vec{x}-\omega t)}\right) \qquad \text{with} \qquad \vec{k} \equiv \tfrac{2\pi}{L}\vec{n}. \tag{10.77}$$

The constant contribution for $\vec{n} = \vec{0}$ can be omitted because it does not contribute to $\vec{E}$ or $\vec{B}$. For $\vec{n} \neq \vec{0}$ the coefficient vectors $\vec{a}(k)$ have to be transversal $\vec{k}\cdot\vec{a}_k = 0$. This condition is solved by linear combinations of two transversal polarization vectors $\vec{e}_{k\alpha}$ with $\alpha = 1,2$ which we choose to be orthonormal,

$$\vec{k}\cdot\vec{e}_{k\alpha} = 0, \qquad \vec{e}_{k\alpha}\cdot\vec{e}_{k\alpha'} = \delta_{\alpha\alpha'} \qquad \Rightarrow \qquad \sum_{\alpha=1,2}(e_{k\alpha})_i(e_{k\alpha})_j = \delta_{ij} - \tfrac{k_i k_j}{k^2} \equiv \delta_{ij}^T. \tag{10.78}$$

With the expansion $\vec{a}_k = \sum_{\alpha=1}^{2} a_{k\alpha}\,\vec{e}_{k\alpha}$ our ansatz becomes

$$\vec{A}(\vec{x},t) = \sum_{\substack{\vec{n}\in\mathbb{Z}^3\\ \vec{n}\neq\vec{0}}}\sum_{\alpha=1,2}\sqrt{\frac{2\pi\hbar c^2}{V\omega}}\left(a_{k\alpha}e^{i(\vec{k}\vec{x}-\omega t)} + a_{k\alpha}^* e^{-i(\vec{k}\vec{x}-\omega t)}\right)\vec{e}_{k\alpha} \tag{10.79}$$

In terms of the vectorpotential the energy of our radiation field is

$$H = \frac{1}{8\pi}\int_V d^3x\,\left(\vec{E}^2 + \vec{B}^2\right) = \frac{1}{8\pi}\int_V d^3x\,\left(\frac{1}{c^2}\left(\frac{\partial\vec{A}}{\partial t}\right)^2 + \left(\nabla\times\vec{A}\right)^2\right) \tag{10.80}$$

Inserting the ansatz (10.79) into this expression the integral can be evaluated and we obtain

$$H = \frac{1}{2}\sum_{\vec{n},\alpha}\hbar\omega\,(a_{k\alpha}a_{k\alpha}^* + a_{k\alpha}^* a_{k\alpha}) \qquad \text{with} \qquad \vec{k} = \frac{2\pi}{L}\,\vec{n}, \quad \omega = c\,|\vec{k}|. \tag{10.81}$$

This form of the Hamilton function reminds us of the harmonic oscillator and also of the Hamiltonian (10.71) of free particles in the occupation number representation. It is hence

natural to interpret the Fourier coefficients $a_{k\alpha}$ as anihilation operators and to replace their complex conjugates by the corresponding creation operators

$$a^*_{k\alpha} \;\rightarrow\; a^\dagger_{k\alpha}, \qquad [a_{k\alpha}, a^\dagger_{k'\alpha'}] = \delta_{\alpha,\alpha'}\delta_{\vec{k},\vec{k}'}. \tag{10.82}$$

This procedure is called *field quantization*, or *second quantization* in contrast to the first quatization in which particle trajectories were replaced by wave functions. Electromagnetism is described by a field already at the classical level, and its quantization is performed by replacing (the Fourier modes of) the classical field by operators.[4]

With the identification of the Fourier coefficients of the electromagnetic field in a box with creation and annihilation operators we interpret each oscillation mode as a harmonic oscillator. According to the Hamilton function (10.81) $\vec{E}^2$ provides the kinetic term and $\vec{B}^2$ plays the role of a harmonic potential. For finite volume we have a discretely infinite sum over polarizations α and wave vectors $\vec{k} \in \frac{2\pi}{L}\mathbb{Z}^3$ of harmonic oscillators. For $L \to \infty$ the Fourier series turns into a Fourier integral and we obtain a continuum of such oscillators.

10.4.2 Interaction of matter and radiation

We are now in the position to compute electromagnetic transitions in atomic physics. Our starting point is Fermi's golden rule

$$P_{i\to f} \;=\; \frac{2\pi}{\hbar}\,\delta(E_i - E_f)\,|\langle f|H_I|i\rangle|^2, \tag{10.86}$$

which we derived in chapter 6. It expresses the transition probability $P_{i\to f}$ per unit time from an initial state $|i\rangle$ to a final state $|f\rangle$ in terms of the matrix element of the interaction Hamiltonian H_I in the interaction picture. We will only work out the leading approximation and neglect

[4] In a more deductive approach, the starting point for the quantization of the electromagnetic field $\vec{A}(x,t)$ is the Lagrange function $L = \int d^3x\mathcal{L}$ with Lagrange density

$$\mathcal{L} = \frac{1}{8\pi}(\vec{E}^2 - \vec{B}^2) = \frac{1}{8\pi}\left(\frac{1}{c^2}\dot{\vec{A}}^2 - (\nabla\times\vec{A})^2\right). \tag{10.83}$$

The canonical momenta π_i conjugate to the dynamical variables A_i are

$$\pi_i = \frac{\partial\mathcal{L}}{\partial\dot{A}_i} = \frac{1}{4\pi c^2}\dot{A}_i = -\frac{1}{4\pi c}E_i. \tag{10.84}$$

By inserting the expansion (10.79) one can show that the commutation relations (10.82) for the Fourier coefficients are equivalent to

$$[A_i(\vec{x},t), \pi_j(\vec{y},t)] = i\hbar\,\delta^T_{ij}(\vec{x}-\vec{y}), \tag{10.85}$$

where $\delta^T_{ij}(\vec{x}-\vec{y})$ is the Fourier transform of the transversal δ-function that was defined in eq. (10.78). The restriction of the δ-function to transversal degrees of freedom is required by the Coulomb gauge condition (10.73). This can be shown to follow from the quantization prescription in the presence of constraints that was developed by Dirac and Bergmann [Dirac]. A theoretical framework that enabled a Lorentz covariant canonical quantization of the full electromagnetic field was only developed in the 1970s.

magnetic interactions with the electron's spin and the order $(eA)^2$ term in the Hamiltonian

$$H = \frac{1}{2m}(\vec{p} - \frac{e}{c}\vec{A})^2 + \ldots \qquad \Rightarrow \qquad H_I = -\frac{e}{2mc}(\vec{p}\vec{A} + \vec{A}\vec{p}) + \ldots, \tag{10.87}$$

where $\vec{p}\vec{A} = \vec{A}\vec{p}$ in the Coulomb gauge.

In the interaction picture the initial and final states are energy eigenstates of the Hamiltonian $H_{mat} + H_{em}$, which factorize into a matter part with energy eigenvalue ε and a photon state in the occupation number representation,

$$|i\rangle = |\lambda_i\rangle \otimes |n_i\rangle, \qquad |f\rangle = |\lambda_f\rangle \otimes |n_f\rangle, \qquad H_{mat}\,|\lambda\rangle = \varepsilon|\lambda\rangle \tag{10.88}$$

where $\lambda = (\varepsilon, \ldots)$ specifies the energy eigenstate of the electron. For the emission or absorption of a single photon it is sufficient to specify the occupation number $n_f = n_i \pm 1$ for the momentum $\vec{k}$ and the polarization α for which we want to compute the probability (10.86). Inserting $-\frac{e}{mc}\vec{p}\vec{A}$ with

$$\vec{A}(\vec{x}, 0) = \sum_{\substack{\vec{n}\in\mathbb{Z}^3 \\ \vec{n}\neq\vec{0}}} \sum_{\alpha=1,2} \sqrt{\frac{2\pi\hbar c^2}{V\omega}} \left(a_{k\alpha} e^{i\vec{k}\vec{x}} + a^\dagger_{k\alpha} e^{-i\vec{k}\vec{x}} \right) \vec{e}_{k\alpha} \tag{10.89}$$

and the matrix elements

$$\langle n_i - 1|a|n_i\rangle = \sqrt{n_i}. \qquad \langle n_i + 1|a^\dagger|n_i\rangle = \sqrt{n_i + 1} \tag{10.90}$$

we obtain the *absorption* probability

$$P_{i\to f} \;=\; \frac{4\pi^2 e^2}{m^2 V\omega}\, \delta(\varepsilon_i + \hbar\omega - \varepsilon_f)\; n_{i,k\alpha} \;\left| \langle \varepsilon_f|\; \vec{p}\,\vec{e}_{k\alpha}\; e^{i\vec{k}\vec{x}}\; |\varepsilon_i\rangle \right|^2 \tag{10.91}$$

and the *emission* probability

$$P_{i\to f} \;=\; \frac{4\pi^2 e^2}{m^2 V\omega}\, \delta(\varepsilon_i - \hbar\omega - \varepsilon_f)\; (n_{i,k\alpha} + 1)\; \left| \langle \varepsilon_f|\; \vec{p}\,\vec{e}_{k\alpha}\; e^{-i\vec{k}\vec{x}}\; |\varepsilon_i\rangle \right|^2. \tag{10.92}$$

For $n_i = 0$ we obtain the probability for spontaneous emission, while the probabilities for absorption and induced emission are proportional to the occupation number.

In the dipol approximation the exponentials $e^{i\vec{k}\vec{x}}$ are replaced by 1. Since $[\vec{x}, H] = \frac{i\hbar}{m}\vec{p}$ the expectation value of $\vec{p}$ is related to the dipol moment by

$$\langle \varepsilon_f|\vec{p}|\varepsilon_i\rangle = \tfrac{im}{\hbar}(\varepsilon_f - \varepsilon_i)\,\langle \varepsilon_f|\vec{x}|\varepsilon_i\rangle \tag{10.93}$$

If we want to compute the life time for an excited state we need to integrate over all momenta and to sum over all polarizations. Since $\vec{k} = \frac{2\pi}{L}\vec{\mu}$ the limit $L \to \infty$ amonts to

$$\frac{1}{V} \sum_{\vec{\mu}\,\in\,\mathbb{Z}^3} \qquad \to \qquad \int \frac{d^3k}{(2\pi)^3} \tag{10.94}$$

The energy conserving δ-function leads to a finite integral over a sphere in momentum space.

10.4.3 Phonons and quasiparticles

As one can hear by knocking on a door the lowest vibration frequencies of a solid are far below the frequencies ω that correspond to excitations of single atoms or molecules. This implies that the smallest energy quanta $\hbar\omega$ that are available in a solid for quantum mechanical processes correspond to excitations that involve the collective motion of a large number of atoms. The particle-like degrees of freedom that enter such a process are called *quasi-particles*. In the case of lattice vibrations of a solid the quasi-particles are called phonons.

For small temperatures anharmonic effects may be neglected and the Hamiltonian has the form

$$H = \sum_{l=1}^{L} \frac{p_l^2}{2m_l} + \frac{1}{2} \sum_{k,l=1}^{L} K_{kl} x_k x_l, \tag{10.95}$$

where m_l are the effective masses of the elementary degrees of freedom and the matrix K_{kl} describes the harmonic forces. Diagonalization yields the normal modes, which correspond to decoupled harmonic oscillators. In terms of the respective creation and annihilation operators the quantum system is hence described by a Hamilton function

$$H = \sum \hbar\omega_i (a_i^\dagger a_i + \frac{1}{2}). \tag{10.96}$$

The number operators $N_i = a_i^\dagger a_i$ count the occupation numbers of the phonon states with wave vector $\vec{k}$ and their dispersion relation $\omega(\vec{k})$ is given by the speed of sound. Many physical properties of solids such as specific heat and thermal conductivity can be describe in terms of phonons, which are bosons with spin zero.

Phonons in a solid are quite analogous to electromagnetic modes in a cavity and we can read the previous quantization procedure backwards and construct a phonon field $\phi(\vec{x}, t) \sim \sum (a_k e^{i(\vec{k}\vec{x}-\omega t)} + a_k^\dagger e^{-i(\vec{k}\vec{x}-\omega t)})$. For certain quantities non-linear interaction terms become important. Creation and annihilation of phonons requires cubic terms ϕ^3, which automatically have a excess of a creation operator or an annihilation operator and hence change the phonon number. Phonon-phonon scattering is described by interaction terms ϕ^4, whose expansion in creation and annihilation operators assumes the form of two-particle operator.