Chapter 4

Introduction to many-body quantum mechanics

4.1 The complexity of the quantum many-body problem

After learning how to solve the 1-body Schrödinger equation, let us next generalize to more particles. If a single body quantum problem is described by a Hilbert space $\mathcal{H}$ of dimension $\dim\mathcal{H} = d$ then N *distinguishable* quantum particles are described by the tensor product of N Hilbert spaces

$$\mathcal{H}^{(N)} \equiv \mathcal{H}^{\otimes N} \equiv \bigotimes_{i=1}^{N} \mathcal{H} \tag{4.1}$$

with dimension d^N.

As a first example, a single spin-1/2 has a Hilbert space $\mathcal{H} = \mathbb{C}^2$ of dimension 2, but N spin-1/2 have a Hilbert space $\mathcal{H}^{(N)} = \mathbb{C}^{2^N}$ of dimension 2^N. Similarly, a single particle in three dimensional space is described by a complex-valued wave function $\psi(\vec{x})$ of the position $\vec{x}$ of the particle, while N distinguishable particles are described by a complex-valued wave function $\psi(\vec{x}_1, \ldots, \vec{x}_N)$ of the positions $\vec{x}_1, \ldots, \vec{x}_N$ of the particles. Approximating the Hilbert space $\mathcal{H}$ of the single particle by a finite basis set with d basis functions, the N-particle basis approximated by the same finite basis set for single particles needs d^N basis functions.

This exponential scaling of the Hilbert space dimension with the number of particles is a big challenge. Even in the simplest case – a spin-1/2 with $d = 2$, the basis for $N = 30$ spins is already of of size $2^{30} \approx 10^9$. A single complex vector needs 16 GByte of memory and will not fit into the memory of your personal computer anymore.

This challenge will be to addressed later in this course by learning about

1. approximative methods, reducing the many-particle problem to a single-particle problem
2. quantum Monte Carlo methods for bosonic and magnetic systems
3. brute-force methods solving the exact problem in a huge Hilbert space for modest numbers of particles

4.2 Indistinguishable particles

4.2.1 Bosons and fermions

In quantum mechanics we assume that elementary particles, such as the electron or photon, are indistinguishable: there is no serial number painted on the electrons that would allow us to distinguish two electrons. Hence, if we exchange two particles the system is still the same as before. For a two-body wave function $\psi(\vec{q}_1, \vec{q}_2)$ this means that

$$\psi(\vec{q}_2, \vec{q}_1) = e^{i\phi}\psi(\vec{q}_1, \vec{q}_2), \tag{4.2}$$

since upon exchanging the two particles the wave function needs to be identical, up to a phase factor $e^{i\phi}$. In three dimensions the first homotopy group is trivial and after doing two exchanges we need to be back at the original wave function[1]

$$\psi(\vec{q}_1, \vec{q}_2) = e^{i\phi}\psi(\vec{q}_2, \vec{q}_1) = e^{2i\phi}\psi(\vec{q}_1, \vec{q}_2), \tag{4.3}$$

and hence $e^{2i\phi} = \pm 1$:

$$\psi(\vec{q}_2, \vec{q}_1) = \pm\psi(\vec{q}_1, \vec{q}_2) \tag{4.4}$$

The many-body Hilbert space can thus be split into orthogonal subspaces, one in which particles pick up a $-$ sign and are called fermions, and the other where particles pick up a $+$ sign and are called bosons.

Bosons

For bosons the general many-body wave function thus needs to be symmetric under permutations. Instead of an arbitrary wave function $\psi(\vec{q}_1, \ldots, \vec{q}_N)$ of N particles we use the symmetrized wave function

$$\Psi^{(S)} = \mathcal{S}_+\psi(\vec{q}_1, \ldots, \vec{q}_N) \equiv \mathcal{N}_S \sum_p \psi(\vec{q}_{p(1)}, \ldots, \vec{q}_{p(N)}), \tag{4.5}$$

where the sum goes over all permutations p of N particles, and $\mathcal{N}_S$ is a normalization factor.

[1] As a side remark we want to mention that in two dimensions the first homotopy group is $\mathbb{Z}$ and not trivial: it matters whether we move the particles clock-wise or anti-clock wise when exchanging them, and two clock-wise exchanges are not the identity anymore. Then more general, anyonic, statistics are possible.

Fermions

For fermions the wave function has to be antisymmetric under exchange of any two fermions, and we use the anti-symmetrized wave function

$$\Psi^{(A)}\mathcal{S}_-\psi(\vec{q}_1,\ldots,\vec{q}_N) \equiv \mathcal{N}_A \sum_p \mathrm{sgn}(p)\psi(\vec{q}_{p(1)},\ldots,\vec{q}_{p(N)}), \tag{4.6}$$

where $\mathrm{sgn}(p) = \pm 1$ is the sign of the permutation and $\mathcal{N}_A$ again a normalization factor.

A consequence of the antisymmetrization is that no two fermions can be in the same state as a wave function

$$\psi(\vec{q}_1,\vec{q}_2) = \phi(\vec{q}_1)\phi(\vec{q}_2) \tag{4.7}$$

since this vanishes under antisymmetrization:

$$\Psi(\vec{q}_1,\vec{q}_2) = \psi(\vec{q}_1,\vec{q}_2) - \psi(\vec{q}_2,\vec{q}_1) = \phi(\vec{q}_1)\phi(\vec{q}_2) - \phi(\vec{q}_2)\phi(\vec{q}_1) = 0 \tag{4.8}$$

Spinful fermions

Fermions, such as electrons, usually have a spin-1/2 degree of freedom in addition to their orbital wave function. The full wave function as a function of a generalized coordinate $\vec{x} = (\vec{q},\sigma)$ including both position $\vec{q}$ and spin σ.

4.2.2 The Fock space

The Hilbert space describing a quantum many-body system with $N = 0, 1, \ldots, \infty$ particles is called the Fock space. It is the direct sum of the appropriately symmetrized single-particle Hilbert spaces $\mathcal{H}$:

$$\bigoplus_{N=0}^{\infty} S_\pm \mathcal{H}^{\otimes n} \tag{4.9}$$

where S_+ is the symmetrization operator used for bosons and S_- is the anti-symmetrization operator used for fermions.

The occupation number basis

Given a basis $\{|\phi_1\rangle,\ldots,|\phi_L\rangle\}$ of the single-particle Hilbert space $\mathcal{H}$, a basis for the Fock space is constructed by specifying the number of particles n_i occupying the single-particle wave function $|f_1\rangle$. The wave function of the state $|n_1,\ldots,n_L\rangle$ is given by the appropriately symmetrized and normalized product of the single particle wave functions. For example, the basis state $|1,1\rangle$ has wave function

$$\frac{1}{\sqrt{2}}\left[\phi_1(\vec{x}_1)\phi_2(\vec{x}_2) \pm \phi_1(\vec{x}_2)\phi_2(\vec{x}_1)\right] \tag{4.10}$$

where the $+$ sign is for bosons and the $-$ sign for fermions.

For bosons the occupation numbers n_i can go from 0 to ∞, but for fermions they are restricted to $n_i = 0$ or 1 since no two fermions can occupy the same state.

The Slater determinant

The antisymmetrized and normalized product of N single-particle wave functions ϕ_i can be written as a determinant, called the Slater determinant

$$\mathcal{S}_- \prod_{i_1}^{N} \phi_i(\vec{x}_i) = \frac{1}{\sqrt{N}} \begin{vmatrix} \phi_1(\vec{x}_1) & \cdots & \phi_N(\vec{x}_1) \\ \vdots & & \vdots \\ \phi_1(\vec{x}_N) & \cdots & \phi_N(\vec{x}_N) \end{vmatrix}. \tag{4.11}$$

Note that while the set of Slater determinants of single particle basis functions forms a basis of the fermionic Fock space, the general fermionic many body wave function is a linear superposition of many Slater determinants and cannot be written as a single Slater determinant. The Hartee Fock method, discussed below, will simplify the quantum many body problem to a one body problem by making the approximation that the ground state wave function can be described by a single Slater determinant.

4.2.3 Creation and annihilation operators

Since it is very cumbersome to work with appropriately symmetrized many body wave functions, we will mainly use the formalism of second quantization and work with creation and annihilation operators.

The annihilation operator $a_{i,\sigma}$ associated with a basis function $|\phi_i\rangle$ is defined as the result of the inner product of a many body wave function $|\Psi\rangle$ with this basis function $|\phi_i\rangle$. Given an N-particle wave function $|\Psi^{(N)}\rangle$ the result of applying the annihilation operator is an $N-1$-particle wave function $|\tilde{\Psi}^{(N)}\rangle = a_i|\Psi^{(N)}\rangle$. It is given by the appropriately symmetrized inner product

$$\tilde{\Psi}(\vec{x}_1, \ldots, \vec{x}_{N-1}) = \mathcal{S}_\pm \int d\vec{x}_N f_i^\dagger(\vec{x}_N)\Psi(\vec{x}_1, \ldots, \vec{x}_N). \tag{4.12}$$

Applied to a single-particle basis state $|\phi_j\rangle$ the result is

$$a_i|\phi_j\rangle = \delta_{ij}|0\rangle \tag{4.13}$$

where $|0\rangle$ is the "vacuum" state with no particles.

The creation operator $a_i^\dagger$ is defined as the adjoint of the annihilation operator a_i. Applying it to the vacuum "creates" a particle with wave function ϕ_i:

$$|\phi_i\rangle = a_i^\dagger|0\rangle \tag{4.14}$$

For sake of simplicity and concreteness we will now assume that the L basis functions $|\phi_i\rangle$ of the single particle Hilbert space factor into $L/(2S+1)$ orbital wave functions $f_i(\vec{q})$ and $2S+1$ spin wave functions $|\sigma\rangle$, where $\sigma = -S, -S+1, ..., S$. We will write creation and annihilation operators $a_{i,\sigma}^\dagger$ and $a_{i,\sigma}$ where i is the orbital index and σ the spin index. The most common cases will be spinless bosons with $S=0$, where the spin index can be dropped and spin-1/2 fermions, where the spin can be up $(+1/2)$ or down $(-1/2)$.

Commutation relations

The creation and annihilation operators fulfill certain canonical commutation relations, which we will first discuss for an orthogonal set of basis functions. We will later generalize them to non-orthogonal basis sets.

For bosons, the commutation relations are the same as that of the ladder operators discussed for the harmonic oscillator (2.62):

$$[a_i, a_j] = [a_i^\dagger, a_j^\dagger] = 0 \tag{4.15}$$

$$[a_i, a_j^\dagger] = \delta_{ij}. \tag{4.16}$$

For fermions, on the other hand, the operators anticommute

$$\begin{aligned} \{a_{j\sigma'}^\dagger, a_{i\sigma}\} = \{a_{i\sigma}^\dagger, a_{j\sigma'}\} &= \delta_{\sigma\sigma'}\delta_{ij} \\ \{a_{i\sigma}, a_{j\sigma'}\} = \{a_{i\sigma}^\dagger, a_{j\sigma'}^\dagger\} &= 0. \end{aligned} \tag{4.17}$$

The anti-commutation implies that

$$(a_i^\dagger)^2 = a_i^\dagger a_i^\dagger = -a_i^\dagger a_i^\dagger \tag{4.18}$$

and that thus

$$(a_i^\dagger)^2 = 0, \tag{4.19}$$

as expected since no two fermions can exist in the same state.

Fock basis in second quantization and normal ordering

The basis state $|n_1, \ldots, n_L\rangle$ in the occupation number basis can easily be expressed in terms of creation operators:

$$|n_1, \ldots, n_L\rangle = \prod_{i=1}^{L} (a_i^\dagger)^{n_i} |0\rangle = (a_1^\dagger)^{n_1} (a_2^\dagger)^{n_2} \cdots (a_L^\dagger)^{n_L} |0\rangle \tag{4.20}$$

For bosons the ordering of the creation operators does not matter, since the operators commute. For fermions, however, the ordering matters since the fermionic creation operators anticommute: and $a_1^\dagger a_2^\dagger|0\rangle = -a_1^\dagger a_2^\dagger|0\rangle$. We thus need to agree on a specific ordering of the creation operators to define what we mean by the state $|n_1, \ldots, n_L\rangle$. The choice of ordering does not matter but we have to stay consistent and use e.g. the convention in equation (4.20).

Once the normal ordering is defined, we can derive the expressions for the matrix elements of the creation and annihilation operators in that basis. Using above normal ordering the matrix elements are

$$a_i|n_1, \ldots, n_i, \ldots, n_L\rangle = \delta_{n_i,1}(-1)^{\sum_{j=1}^{i-1} n_i}|n_1, \ldots, n_i - 1, \ldots, n_L\rangle \tag{4.21}$$

$$a_i^\dagger|n_1, \ldots, n_i, \ldots, n_L\rangle = \delta_{n_i,0}(-1)^{\sum_{j=1}^{i-1} n_i}|n_1, \ldots, n_i + 1, \ldots, n_L\rangle \tag{4.22}$$

where the minus signs come from commuting the annihilation and creation operator to the correct position in the normal ordered product.

4.2.4 Nonorthogonal basis sets

In simulating the electronic properties of atoms and molecules below we will see that the natural choice of single particle basis functions centered around atoms will necessarily give a non-orthogonal set of basis functions. This is no problem, as long as the definition of the annihilation and creation operators is carefully generalized. For this generalization it will be useful to introduce the fermion field operators $\psi^\dagger_\sigma(\vec{r})$ and $\psi_\sigma(\vec{r})$, creating and annihilating a fermion localized at a single point $\vec{r}$ in space. Their commutation relations are simply

$$\begin{aligned} \{\psi^\dagger_{\sigma'}(\vec{r}), \psi_\sigma(\vec{r'})\} = \{\psi^\dagger_\sigma(\vec{r}), \psi_{\sigma'}(\vec{r'})\} &= \delta_{\sigma\sigma'}\delta(\vec{r}-\vec{r'}) \\ \{\psi_\sigma(\vec{r}), \psi_{\sigma'}(\vec{r'})\} = \{\psi^\dagger_\sigma(\vec{r}), \psi^\dagger_{\sigma'}(\vec{r'})\} &= 0. \end{aligned} \tag{4.23}$$

The scalar products of the basis functions define a matrix

$$S_{ij} = \int d^3\vec{r} f^*_i(\vec{r}) f_j(\vec{r}), \tag{4.24}$$

which is in general *not* the identity matrix. The associated annihilation operators $a_{i\sigma}$ are again defined as scalar products

$$a_{i\sigma} = \sum_j (S^{-1})_{ij} \int d^3\vec{r} f^*_j(\vec{r}) \psi_\sigma(\vec{r}). \tag{4.25}$$

The non-orthogonality causes the commutation relations of these operators to differ from those of normal fermion creation- and annihilation operators:

$$\begin{aligned} \{a^\dagger_{i\sigma}, a_{j\sigma'}\} &= \delta_{\sigma\sigma'}(S^{-1})_{ij} \\ \{a_{i\sigma}, a_{j\sigma'}\} = \{a^\dagger_{i\sigma}, a^\dagger_{j\sigma'}\} &= 0. \end{aligned} \tag{4.26}$$

Due to the non-orthogonality the adjoint $a^\dagger_{i\sigma}$ does *not* create a state with wave function f_i. This is done by the operator $\hat{a}^\dagger_{i\sigma}$, defined through:

$$\hat{a}^\dagger_{i\sigma} = \sum_j S_{ji} a^\dagger_{i\sigma}, \tag{4.27}$$

which has the following simple commutation relation with $a_{j\sigma}$:

$$\{\hat{a}^\dagger_{i\sigma}, a_{j\sigma}\} = \delta_{ij}. \tag{4.28}$$

The commutation relations of the $\hat{a}^\dagger_{i\sigma}$ and the $\hat{a}_{j\sigma'}$ are:

$$\begin{aligned} \{\hat{a}^\dagger_{i\sigma}\hat{a}_{j\sigma'}\} &= \delta_{\sigma\sigma'}S_{ij} \\ \{\hat{a}_{i\sigma}, \hat{a}_{j\sigma'}\} = \{\hat{a}^\dagger_{i\sigma}, \hat{a}^\dagger_{j\sigma'}\} &= 0. \end{aligned} \tag{4.29}$$

We will need to keep the distinction between a and $\hat{a}$ in mind when dealing with non-orthogonal basis sets.