Lecture 3

Learning goals

- To have a vague idea how to describe many-body physics with wavefunctions; the Hartree-Fock model as an example.
- To understand the fundamental difference between bosons and fermions.
- To learn that wavefunctions of bosons (fermions) must be (anti)symmetrized.
- To understand why number states (Fock states) are useful in describing many-body quantum systems, to learn how bosonic annihilation and creation operators act on them and how the Hamiltonian can be expressed in terms of these operators.

6 Hartree-Fock Model

Literature: R.L. Liboff, Introductory Quantum Mechanics (Fourth edition) (Addison Wesley), Chapter 13.10

The Hartree-Fock self-consistent model describes *in an approximate way* the effect of interactions on a quantum system. In the example considered here, it takes into account the effects on one atomic electron caused by the other atomic electrons and the nucleus. In general, the term Hartree-Fock refers to this type of (simplified) quantum description of interacting particles. Note that exact solution (solving the Schrödinger equation/diagonalizing the Hamiltonian) of interacting quantum systems of many particles is usually extremely hard (for large number of particles; 2-4 particles can be done easily). The Hartree-Fock description will be considered again when we study second quantization. Later in the course we will consider interacting quantum many-body systems, where Hartree-Fock descriptions alone is not sufficient.

The ingredients of the model are the following assumptions:
1) Each electron moves in a central field equal to the nuclear potential and that due to the charge densities of the remaining atomic electrons.
2) The Schrödinger equation is solved for each electron in its own central field, and resulting wavefunctions are made **self-consistent** with the fields from which they are calculated.
3) The atomic wavefunction is a product of single-electron orthonormalized wavefunctions:

$$\Psi\left(\mathbf{r}_1,\ldots,\mathbf{r}_Z\right)=\varphi_1\left(\mathbf{r}_1\right)\ldots\varphi_Z\left(\mathbf{r}_Z\right). \tag{6.1}$$

With the statements 1) and 2):

$$\hat{H}_k\varphi_k\left(\mathbf{r}_k\right)=E_k\varphi_k\left(\mathbf{r}_k\right), \tag{6.2}$$

where

$$\hat{H}_k\equiv\left[-\frac{\hbar^2\nabla_k^2}{2m}+W\left(\mathbf{r}_k\right)\right] \tag{6.3}$$

$$W\left(\mathbf{r}_k\right)=V_C\left(\mathbf{r}_k\right)+V_k\left(\mathbf{r}_k\right) \tag{6.4}$$

$$V_C(\mathbf{r}_k) \equiv -\frac{Ze^2}{4\pi\epsilon_0 r_k} \tag{6.5}$$

$$V_k(\mathbf{r}_k) = \frac{1}{4\pi\epsilon_0}\int \sum_{j\neq k} |\varphi_j(\mathbf{r}_j)|^2 \frac{e^2}{r_{jk}} d\mathbf{r}_j \tag{6.6}$$

$$r_{jk} = |\mathbf{r}_j - \mathbf{r}_k| \tag{6.7}$$

Spin-orbit effects are neglected. The above means that there are Z simultaneous nonlinear integrodifferential equations for the Z functions (Z electrons). The solution is an iterative scheme:
1. Approximate the central potential

$$W(\mathbf{r}_k) \longrightarrow W^{(1)}(\mathbf{r}_k) \tag{6.8}$$

2. Electron wavefunctions calculated using that

$$\left[-\frac{\hbar^2\nabla_k^2}{2m} + W^{(1)}(\mathbf{r}_k)\right]\varphi_k^{(1)}(\mathbf{r}_k) = E_k^{(1)}\varphi_k^{(1)}(\mathbf{r}_k) \tag{6.9}$$

3. Charge densities are calculated, to be used in calculating the potential in Equation (6.6)

$$e^2\left|\varphi_k^{(1)}(\mathbf{r}_k)\right|^2 \tag{6.10}$$

4. Second order iteration atomic potential becomes, see Equation (6.4)

$$W^{(2)}(\mathbf{r}_k) \tag{6.11}$$

Repeated until $\left|W^{(n+1)}(\mathbf{r}_k) - W^{(n)}(\mathbf{r}_k)\right| < \varepsilon$.

Note: this contained only the Hartree contribution. The Fock contribution is the exchange of indistinguishable particles. Here it is proportional to $\int \varphi_1(\mathbf{r}_j)\,\varphi_2(\mathbf{r}_k)\,\frac{1}{r_{jk}}$ and may be neglected if the overlap of $\varphi_1$and φ_2 is small.

7 Second quantization

Literature: F. Schwabl, Advanced Quantum Mechanics, Third edition (Springer), Chapters 1.2-1.4

Second quantization is a convenient technique to take into account quantum statistics in many-body systems by using operators. Here we first have a look at how to describe many-body systems without operators, just considering wavefunctions, and then introduce the operators.

F. Schwabl, Chapter 1.1 is background material, not part of the course, where a mathematically more rigorous treatment of the permutation symmetry presented below can be found.

The Hamiltonian for N identical particles

$$H = H(\mathbf{1}, \mathbf{2}, \ldots, \mathbf{N}) \tag{7.1}$$

is symmetric with respect to the 1, ..., N particles. Here $\mathbf{1} = \mathbf{x}_1, \sigma_1$ denotes both position and spin. A meaningful Hamiltonian (7.1) has to be symmetric, since for identical particles physically observable quantities such as the energy (Hamiltonian) have to be invariant under permutations of the particles. If one permutes particles in an eigenfunction of the Hamiltonian (7.1), the permuted function also has to be an eigenfunction of the Hamiltonian (7.1) and with the same energy. Therefore, the permuted wavefunctions are experimentally indistinguishable.

But what else can be said about the wavefunction of a system? A wavefunction is not a directly observable quantity in the same way as physical observables. What happens to the wavefunction under permutations? Write the wavefunction as

$$\Psi = \Psi(\mathbf{1}, \mathbf{2}, \ldots, \mathbf{N}). \tag{7.2}$$

Apply a permutation:

$$P_{ij}\Psi(\ldots, \mathbf{i}, \ldots, \mathbf{j}, \ldots) = \Psi(\ldots, \mathbf{j}, \ldots, \mathbf{i}, \ldots) \tag{7.3}$$

It is natural to demand that doing the same perturbation twice, one should return to the initial state:

$$P_{ij}^2 = 1. \tag{7.4}$$

Therefore, the eigenvalues of the permutation operator (7.3) are:

$$p_{ij} = \pm 1. \tag{7.5}$$

What should the symmetry properties of a wavefunction be? In principle, there are N! different permutations, and one could make any linear combinations from these.

EXPERIMENTAL FACT: There are two types of particles, bosons and fermions, for which the wavefunctions are either totally symmetric or totally antisymmetric, respectively:

$$P_{ij}\Psi_{s,a}(\ldots, \mathbf{i}, \ldots, \mathbf{j}, \ldots) = \pm\Psi_{s,a}(\ldots, \mathbf{j}, \ldots, \mathbf{i}, \ldots). \tag{7.6}$$

Symmetric wavefunction – spin integer particles.
Antisymmetric wavefunction – spin half integer particles.
This relation between symmetry and spin can be proved with relativistic quantum field theory (not part of the course). However, the fact that there are only symmetric and antisymmetric wavefunctions cannot be proven, it is simply what the experiments tell us about the nature.

Let us now write down completely (anti)symmetric basis states, with which any (fermion) boson system can then be described. Notation:

$$|i_\alpha\rangle_\beta \equiv \varphi_\alpha(\mathbf{x}_\beta, \sigma_\beta) \tag{7.7}$$

α refers to a single-particle state, β refers to a particle.
Assume that the single particle states are complete and orthonormal.
Basis states for an N-particle system:

$$|i_1, \ldots, i_\alpha, \ldots, i_N\rangle = |i_1\rangle_1 \ldots |i_\alpha\rangle_\alpha \ldots |i_N\rangle_N \tag{7.8}$$

(Anti)symmetric basis states:

$$S_{\pm} |i_1, i_2, \ldots, i_N\rangle \equiv \frac{1}{\sqrt{N!}} \sum_P (\pm 1)^P P |i_1, i_2, \ldots, i_N\rangle \tag{7.9}$$

Sum over all permutations P (there are $N!$ of them). For Fermions, get $\pm$ depending on odd/even # of permutations.

For two particles:

$$|\Psi_{s,a}\rangle = \frac{1}{\sqrt{2}} \left[|1\rangle_1 |2\rangle_2 \pm |2\rangle_1 |1\rangle_2 \right] \tag{7.10}$$

For N particles: a nightmare. Let us do the **second quantization** in order to simplify life.
QUIZ
QUIZ
QUIZ

7.1 Bosons

For bosons, it is possible to have, e.g., $|1\rangle_1 |1\rangle_2$, that is two particles occupying the same state. Any fully symmetric, normalized state for bosons can be specified with occupation numbers, telling how many particles are in a specific state.

Symmetric basis states:

$$|n_1, n_2, \ldots\rangle = S_+ |i_1, i_2, \ldots, i_N\rangle \frac{1}{\sqrt{n_1! n_2! \ldots}} \tag{7.11}$$

n_i is the number of particles in state i
$\frac{1}{\sqrt{n_1! n_2! \ldots}}$ is the normalisation since the same states occur, e.g. $|1\rangle_1 |1\rangle_2 + |1\rangle_1 |1\rangle_2$. For instance $\varphi_1(x_1)\varphi_1(x_2)\varphi_2(x_3)$ is the same as $\varphi_1(x_2)\varphi_1(x_1)\varphi_2(x_3)$ but different from $\varphi_1(x_3)\varphi_1(x_2)\varphi_2(x_1)$.

Note: sum of all occupation numbers must be the total number of particles:

$$\sum_{i=1}^{\infty} n_i = N \tag{7.12}$$

The idea in second quantization is: let us just use the states $|n_1, n_2, \ldots\rangle$, find operators that act in a convenient way on these states, and write all the physics of the problem in terms of them. In this way, we can avoid worrying about the permutations; the effect of permutations is "hidden" in the states $|n_1, n_2, \ldots\rangle$ and in the way operators act on them.

7.1.1 Fock space

The Fock space is a space where the basis vectors are defined by the occupation numbers. The states that span the space must have

Orthogonality:

$$\langle n_1, n_2, \ldots | n_1', n_2', \ldots\rangle = \delta_{n_1 n_1'} \delta_{n_2 n_2'} \ldots \tag{7.13}$$

Completeness:

$$\sum_{n_1, n_2, \ldots} |n_1, n_2, \ldots\rangle \langle n_1, n_2, \ldots| = \hat{1} \tag{7.14}$$

Some operators, like x and p, acting on an N-particle state leave it as an N-particle state. But there are also operators that can change the occupation number.

Let us define *the annihilation and creation operators.* As will be seen, other operators can be expressed in terms of these. The point with annihilation and creation operators is that they act in a particularly convenient way on the states of the Fock space.

The creation operator is:

$$a_i^\dagger \left|\ldots, n_i, \ldots\right\rangle = \sqrt{n_i + 1}\left|\ldots, n_i + 1, \ldots\right\rangle \tag{7.15}$$

The adjoint (annihilation) operator:

$$\left\langle\ldots, {n'}_i, \ldots\right| a_i = \sqrt{{n'}_i + 1}\left\langle\ldots, {n'}_i + 1, \ldots\right| \tag{7.16}$$

$$\Rightarrow \left\langle\ldots, {n'}_i, \ldots\right| a_i \left|\ldots, n_i, \ldots\right\rangle = \sqrt{n_i}\delta_{{n'}_i+1, n_i} \tag{7.17}$$

$$\Rightarrow a_i \left|\ldots, n_i, \ldots\right\rangle = \sqrt{n_i}\left|\ldots, n_i - 1, \ldots\right\rangle, \qquad for \quad n_i \geq 1 \tag{7.18}$$

$$a_i \left|\ldots, n_i = 0, \ldots\right\rangle = 0 \tag{7.19}$$

These relations together with the completeness relation mean that the operators fulfill the Bose commutation relations (to show this is an exercise, see **Exercise Set 3**):

$$[a_i, a_j] = 0, \qquad \left[a_i^\dagger, a_j^\dagger\right] = 0, \qquad \left[a_i, a_j^\dagger\right] = \delta_{ij}. \tag{7.20}$$

Now, we can construct all states by using the annihilation and creation operators and starting from the ground state. This is also called the vacuum state, however, it is not necessarily the same as physical vacuum. The vacuum state could be, for instance, a state where no particle moves. Then the creation operator could create one particle that actually moves with some velocity. Sometimes, of course, the vacuum state can be real vacuum, such as in the case of quantized electromagnetic field, where in the vacuum state there are no photons, and the creation operator creates photons.

Ground (vacuum) state:

$$\left|0\right\rangle \equiv \left|0, 0, \ldots\right\rangle \tag{7.21}$$

Single-particle states:

$$a_i^\dagger \left|0\right\rangle, \qquad \ldots \tag{7.22}$$

Two-particle states:

$$\frac{1}{\sqrt{2}}\left(a_i^\dagger\right)^2 \left|0\right\rangle, \qquad a_i^\dagger a_j^\dagger \left|0\right\rangle, \qquad \ldots \tag{7.23}$$

N-particle states:

$$\left|n_1, n_2, \ldots\right\rangle = \frac{1}{\sqrt{n_1! n_2! \ldots}}\left(a_1^\dagger\right)^{n_1}\left(a_2^\dagger\right)^{n_2} \ldots \left|0\right\rangle, \ldots \tag{7.24}$$

Normalization:

$$a^\dagger |n-1\rangle = \sqrt{n}\,|n\rangle \tag{7.25}$$

$$|n\rangle = \frac{1}{\sqrt{n}} a^\dagger |n-1\rangle \tag{7.26}$$

QUIZ
QUIZ
QUIZ

7.1.2 The particle number operator

Occupation number in state $|i\rangle$:

$$\hat{n}_i = a_i^\dagger a_i \tag{7.27}$$

Total number of particles:

$$\hat{N} = \sum_i \hat{n}_i; \tag{7.28}$$

$$\hat{N} |n_1, n_2, \ldots\rangle = N |n_1, n_2, \ldots\rangle \tag{7.29}$$

Consider a noninteracting system, where $|i\rangle$ are the eigenstates of the Hamiltonian with energy E_i. Then it is easy to write the Hamiltonian

$$H_0 = \sum_i \hat{n}_i E_i \tag{7.30}$$

$$\Rightarrow H_0 |n_1, n_2, \ldots\rangle = \left(\sum_i n_i E_i \right) |n_1, n_2, \ldots\rangle \tag{7.31}$$

The commutation and other properties of the number operator are equal to those in the case of a harmonic oscillator.

7.1.3 General single- and many-particle operators

In the second quantized formalism, we aim at a description where everything, the states as well as the Hamiltonian and other operators, is expressed in terms of the creation and annihilation operators.

An example of a single-particle operator: the kinetic energy $\frac{\mathbf{p}^2}{2m}$ or a potential $U(x)$:

$$\mathcal{A}_\beta = \frac{\mathbf{p}_\beta^2}{2m}, \qquad U(\mathbf{x}_\beta) \tag{7.32}$$

Total operator (sum of single-particle operators for all particles):

$$T = \mathcal{A}_1 + \mathcal{A}_2 + \ldots + \mathcal{A}_N = \sum_\beta \mathcal{A}_\beta \tag{7.33}$$

Here β is the particle label, i is the state label.
Matrix elements:

$$\mathcal{A}_{ij} = \langle i | \mathcal{A} | j \rangle \tag{7.34}$$

so

$$\mathcal{A} = \sum_{i,j} \mathcal{A}_{ij} \left|i\right\rangle \left\langle j\right| \tag{7.35}$$

The total operator (7.33) becomes

$$T = \sum_{i,j} \mathcal{A}_{ij} \sum_{\beta=1}^{N} \left|i\right\rangle_{\beta\,\beta} \left\langle j\right| \tag{7.36}$$

This can be represented in terms of the creation and annihilation operators:

$$\sum_{\beta} \left|i\right\rangle_{\beta\,\beta} \left\langle j\right| \left|\ldots, n_i, \ldots, n_j, \ldots\right\rangle \tag{7.37}$$

($i \neq j$. Use notation $\left|i_1, i_2, \ldots, i_N\right\rangle$ from (7.11))

$$= \sum_{\beta} \left|i\right\rangle_{\beta\,\beta} \left\langle j\right| S_+ \left|i_1, i_2, \ldots, i_N\right\rangle \frac{1}{\sqrt{n_1! n_2! \ldots}} \tag{7.38}$$

($\sum_\beta \left|i\right\rangle_{\beta\,\beta} \left\langle j\right|$ is symmetric, so it commutes with S_+)

$$= S_+ \sum_{\beta} \left|i\right\rangle_{\beta\,\beta} \left\langle j\right| \left|i_1, i_2, \ldots, i_N\right\rangle \frac{1}{\sqrt{n_1! n_2! \ldots}} \tag{7.39}$$

from this it follows (shown in **Exercise Set 3**) (return to notation $\left|\ldots, n_i, \ldots, n_j, \ldots\right\rangle$)

$$= n_j \sqrt{n_i + 1} \frac{1}{\sqrt{n_j}} \left|\ldots, n_i + 1, \ldots, n_j - 1, \ldots\right\rangle$$

$$= \sqrt{n_j}\sqrt{n_i + 1} \left|\ldots, n_i + 1, \ldots, n_j - 1, \ldots\right\rangle$$

$$= a_i^\dagger a_j \left|\ldots, n_i, \ldots, n_j, \ldots\right\rangle \tag{7.40}$$

So, compare rows (7.37) and (7.40) above:

$$\Rightarrow \sum_{\beta=1}^{N} \left|i\right\rangle_{\beta\,\beta} \left\langle j\right| = a_i^\dagger a_j. \tag{7.41}$$

Thus any single particle operator (7.36) can be expressed as

$$T = \sum_{i,j} \mathcal{A}_{ij} a_i^\dagger a_j, \tag{7.42}$$

where $\mathcal{A}_{ij} = \left\langle i\right| \mathcal{A} \left|j\right\rangle$. If $\mathcal{A}_{ij} = E_i \delta_{ij} \Rightarrow$

$$H_0 = \sum_i E_i a_i^\dagger a_i. \tag{7.43}$$

QUIZ
QUIZ
QUIZ

In the same way, for two-particle operators

$$F = \frac{1}{2} \sum_{\alpha \neq \beta} \hat{f}^{(2)} \left(\mathbf{x}_\alpha, \mathbf{x}_\beta \right) \tag{7.44}$$

one can first express the operator in the basis of $|i\rangle_\beta$:

$$F = \frac{1}{2} \sum_{i,j,k,m} \langle i,j| \hat{f}^{(2)} |k,m\rangle \sum_{\beta \neq \alpha}^{N} |i\rangle_\alpha |j\rangle_{\beta\,\alpha} \langle k|_\beta \langle m| , \tag{7.45}$$

where the symmetry of $\hat{f}^{(2)}$ that makes the matrix element independent of α and β was used. Now one can introduce the operators using the relation 7.41 (it is a useful trick to add and substract the term $\alpha = \beta$ to/from the formula). The result becomes

$$F = \frac{1}{2} \sum_{i,j,k,m} \langle i,j| \hat{f}^{(2)} |k,m\rangle \, a_i^\dagger a_j^\dagger a_m a_k, \tag{7.46}$$

where

$$\langle i,j| \hat{f}^{(2)} |k,m\rangle = \int d\mathbf{x} \int d\mathbf{y} \varphi_i^* \left(\mathbf{x} \right) \varphi_j^* \left(\mathbf{y} \right) f^{(2)} \left(\mathbf{x}, \mathbf{y} \right) \varphi_k \left(\mathbf{x} \right) \varphi_m \left(\mathbf{y} \right). \tag{7.47}$$