

Second Quantization

- First quantization in physics refers to the property of particles that certain operators do not commute

$$[x, p_x] = i\hbar \quad (1)$$

$$[L_x, L_y] = i\hbar L_z \quad (2)$$

In the first quantization formalism, the wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ has **fixed number** of the particles, N , and is c-number which is operated by other operators like Hamiltonian.

- Second quantization **quantizes particles**. The basic idea is that all particles (electrons and bosons mediating interaction) can be quantized and represented by operators rather than c-numbers.

In the second quantization formalism, the number of particle is not fixed and the information of the single particle bases are incorporated in the operators.

Let us consider a system on N identical particles described in the Schroedinger representation by the Hamiltonian

$$H(x_1, x_2, \dots, x_N) = \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_i V_{external}(x_i) + \frac{1}{2} \sum_{i \neq j} U_{Coulomb}(x_i, x_j) \quad (3)$$

Here x_i incorporates position and spin of the particles (\mathbf{r}_i, s_i) .

The many-body Schroedinger equation is

$$H(x_1, x_2, \dots, x_N) \Psi(x_1, x_2, \dots, x_N) = i\hbar \frac{\partial}{\partial t} \Psi(x_1, x_2, \dots, x_N) \quad (4)$$

To get to the second quantized form of H , we will first introduce an "intermediate" representation - occupation number representation. Then it will become clear how to simplify the notation by introducing operators for creating or destroying a particle.

To solve one particle problem, we can expand the solution $\psi(x)$ in certain complete set of functions. For N body problem, we need a complete set of N -particle wave functions $\Phi(x_1, x_2, \dots, x_N)$.

We will construct these wave functions as a properly symmetrized product of one-particle wave functions $u_k(x)$ which form a complete orthonormal set

$$\int u_{k'}^*(x)u_k(x)dx = \delta_{kk'} \quad \textit{orthonormality} \quad (5)$$

$$\sum_k u_k^*(x')u_k(x) = \delta(x - x') \quad \textit{completeness} \quad (6)$$

The function Φ is then given by

$$\Phi_{k_1, k_2, \dots, k_N} = \mathcal{S}u_{k_1}(x_1)u_{k_2}(x_2) \cdots u_{k_N}(x_N) \quad (7)$$

where $\mathcal{S} = \frac{1}{n!} \sum P$ in Bose statistics and $\mathcal{S} = \frac{1}{n!} \sum (-1)^p P$ in Fermi statistics and the summation is over all $n!$ possible permutations of the coordinates x_1, x_2, \dots, x_N and p is the order of the permutation.

Basic idea: Rather than labeling Φ by the quantum numbers $\{k_1, k_2, \dots, k_N\}$ we may specify the state by stating how many times each single particle state enters the product - how many times is occupied. Let this occupation number be n_k for state k . **The set of numbers n_1, n_2, \dots, n_k uniquely determines the symmetrized state $\Phi_{n_1, n_2, \dots, n_k}$.**

Total number of particles in the system is clearly $N = \sum_k n_k$.

The numbers n_k are

- Fermions - n_k is either 0 or one
- Bosons - n_k is any positive integer number or zero

The functions $\Phi_{n_1, n_2, \dots, n_k}(x_1, x_2, \dots, x_k)$ form a **complete orthonormal set of N-particle functions**. The orthohonality condition is

$$\langle \Phi_{n'_1, n'_2, \dots, n'_n} | \Phi_{n_1, n_2, \dots, n_n} \rangle = \delta_{n'_1 n_1} \delta_{n'_2 n_2} \cdots \delta_{n'_n n_n} \quad (8)$$

$$= \int \cdots \int dx_1 \cdots dx_n \Phi_{n'_1, n'_2, \dots, n'_n}^*(x_1, x_2, \dots, x_n) \Phi_{n_1, n_2, \dots, n_n}(x_1, x_2, \dots, x_n) \quad (9)$$

(10)

The total Schroedinger wave function may be expanded in the complete set of the functions

$\Phi_{n_1, n_2, \dots, n_k}$

$$\Psi(x_1, x_2, \dots, x_n, t) = \sum A(n_1, n_2, \dots, n_n, t) \Phi_{n_1, n_2, \dots, n_n}(x_1, x_2, \dots, x_n) \quad (11)$$

The coefficients $A(n_1, n_2, \dots, n_n, t)$ are the wave function in the occupation number representation. Their norm gives probability of finding n_k particles in state k .

Now we are redy for the second quantization!

In second quantization, we introduce a set of operators a_k and a_k^\dagger defined by

$$a_k^\dagger \Phi_{n_1, \dots, n_k, \dots}(x_1, \dots, x_n) = \sqrt{n_k + 1} \Phi_{n_1, \dots, n_k + 1, \dots}(x_1, \dots, x_n) \quad (12)$$

$$a_k \Phi_{n_1, \dots, n_k, \dots}(x_1, \dots, x_n) = \sqrt{n_k} \Phi_{n_1, \dots, n_k - 1, \dots}(x_1, \dots, x_n) \quad (13)$$

Operator a_k^\dagger (creation operator) adds one particle in the state k and a_k (destruction operator) destroys a particle in state k .

From the above definition follows that the operator $a_k^\dagger a_k$ counts number of particles

$$a_k^\dagger a_k \Phi_{n_1, \dots, n_k, \dots}(x_1, \dots, x_n) = n_k \Phi_{n_1, \dots, n_k, \dots}(x_1, \dots, x_n) \quad (14)$$

so that the total number of particles is $N = \sum_k a_k^\dagger a_k$.

Φ is symmetric for bosons and antisymmetric for fermions. With this in mind, we can derive the commutation relations for operators from the above definition. For bosons we have

$$\left[a_k, a_{k'}^\dagger \right] = \delta_{kk'} \quad \left[a_k, a_{k'} \right] = 0 \quad \left[a_k^\dagger, a_{k'}^\dagger \right] = 0 \quad (15)$$

Similarly for fermions it follows

$$\{ a_k, a_{k'}^\dagger \} = \delta_{kk'} \quad \{ a_k, a_{k'} \} = 0 \quad \{ a_k^\dagger, a_{k'}^\dagger \} = 0 \quad (16)$$

The power of the second quantization is in possibility to represent any operator in terms of creation and destruction operator for particles (one can have however many types of particles).

The above Hamiltonian can be shown to become (see standard text books, for example Landau, Schrieffer, Abrikosov, ...)

$$H = \sum_{kk'} \langle k|H_0|k'\rangle a_k^\dagger a_{k'} + \frac{1}{2} \sum_{k_1, k_2, k_3, k_4} \langle k_1 k_2|U_{Coulomb}|k_3 k_4\rangle a_{k_1}^\dagger a_{k_2}^\dagger a_{k_4} a_{k_3} \quad (17)$$

where

$$\langle k|H_0|k'\rangle = \int u_k^*(x) \left\{ \frac{p^2}{2m} + V_{ext}(x) \right\} u_{k'}(x) dx \quad (18)$$

$$\equiv \int u_k^*(x) \left\{ -\frac{\hbar^2 \nabla^2}{2m} + V_{ext}(x) \right\} u_{k'}(x) dx$$

$$\langle k_1 k_2|U_{Coulomb}|k_3 k_4\rangle = \int \int u_{k_1}^*(x) u_{k_2}^*(x') U_{Coulomb}(x - x') u_{k_3}(x) u_{k_4}(x') dx dx'$$

One can prove the above identity by checking all possible matrix elements $\langle \Phi|H|\Phi'\rangle$ where Φ and Φ' differ in occupation of k, k', k_1, \dots, k_4 as the above equation dictates.

We will check only the diagonal elements, i.e., $\langle \Phi | H | \Phi \rangle$ because they are equivalent to the *Hartree Fock* approximation. In another words, *Hartree Fock approximation is "the best" approximation in the Hilbert subspace spanned by a single Slater determinant.*

What is $\langle \Phi | H | \Phi \rangle$?

$$\langle \Phi_{n_1 \dots n_i \dots} | H_0(x_i) | \Phi_{n_1, \dots, n_i, \dots} \rangle = \int dx u_i(x)^* \left\{ -\frac{\hbar^2 \nabla^2}{2m} + V_{ext}(x) \right\} u_i(x) dx \quad (19)$$

$$\langle \Phi_{n_1 \dots n_i \dots n_j \dots} | U_C(x_i - x_j) | \Phi_{n_1, \dots, n_{i'}, \dots n_{j'}, \dots} \rangle = \int dx \int dx' u_i^*(x) u_j^*(x') U_C(x - x') u_i(x) u_j(x') \quad (20)$$

$$- \int dx \int dx' u_i^*(x) u_j^*(x') U_C(x - x') u_j(x) u_i(x') \quad (21)$$

And the Hamiltonian in this "single determinant" approximation or Hartree-Fock approximation becomes

$$H = \sum_i \langle i | H_0(x_i) | i \rangle \langle a_i^\dagger a_i \rangle + \frac{1}{2} \sum_{i,j} \langle ij | U_{Coulomb}(x_i - x_j) | ij \rangle \langle a_i^\dagger a_i \rangle \langle a_j^\dagger a_j \rangle \quad (22)$$

$$-\frac{1}{2} \sum_{i,j} \langle ij | U_{Coulomb}(x_i - x_j) | ji \rangle \langle a_i^\dagger a_j \rangle \langle a_j^\dagger a_i \rangle \quad (23)$$

Finally, the field operator is the destruction operator in position base (\mathbf{r} instead of \mathbf{k}). The field operator is usually written as $a_{\mathbf{k}} \rightarrow \Psi(\mathbf{r})$ and $a_{\mathbf{k}}^\dagger \rightarrow \Psi(\mathbf{r})^\dagger$. The commutation relation in this case are

$$\{\Psi(\mathbf{r}), \Psi(\mathbf{r}')\} = \delta(\mathbf{r} - \mathbf{r}') \quad (24)$$

and the Hamiltonian looks very simple

$$H = \int d\mathbf{r} \Psi^\dagger(\mathbf{r}) \left\{ -\frac{\hbar^2 \nabla^2}{2m} + V_{ext}(x) \right\} \Psi(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \Psi^\dagger(\mathbf{r}) \Psi^\dagger(\mathbf{r}') U_C(\mathbf{r} - \mathbf{r}') \Psi(\mathbf{r}') \Psi(\mathbf{r})$$

This is many times the starting point of our derivation (approximation).